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The Role of Crystals in the Elasticity of Semicrystalline Thermoplastic Elastomers.

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The role of crystals in the elasticity of semicrystalline polymers is discussed in the case of syndiotactic polypropylene, which provides an example of a thermoplastic elastomer with a degree of crystallinity that can be tailored by changing and controlling the stereoregularity. This can be achieved using metallocene catalysts with different structures and stereoselectivity. The comparison of crystallization and physical properties of samples of syndiotactic polypropylene of different stereoregularity, with *rrrr* pentad concentrations being variable in the wide range 26−96%, prepared with different catalysts, has shown that syndiotactic polypropylenes present different types of elastic behavior, depending on the degree of crystallinity. For the most-stereoregular and crystalline samples with high melting temperatures, crystals actively participate to the elastic response of the material and elasticity has a mainly enthalpic character attributable to the metastability of the trans-planar form III that transforms into the more-stable helical form II during elastic recovery. For less-crystalline samples, with low melting temperatures, elasticity has instead a pure entropic origin as in conventional thermoplastic elastomers, and crystals act only as knots of the physical elastomeric network.

Introduction

Rubber elasticity is a peculiar property of polymeric materials and is generally defined as being a property of the amorphous phase. Elastomers are high-molecular-weight polymers that possess chemical and/or physical cross-linking. For industrial applications, the temperature at which the elastomers are used must be above the glass transition temperature (to allow for full chain mobility), and in its normal unextended state an elastomer should be amorphous. The restoring force, after elongation, is largely entropic. As the material is stretched, the chains in random coil conformation are forced to occupy more-ordered positions in more-extended conformations. On release of the applied force, the chains tend to return to a more-random state. The gross mobility of entire chains must be low. The cohesive energy forces between chains of elastomers permit rapid, easy extension. In its extended state, an elastomeric chain exhibits a high tensile strength, whereas at low extension, it has a low modulus. Polymers with a low cross-link density usually meet the desired properties requirements. After deformation, the material returns to its original shape because of the cross-linking.[1]

Elastomeric materials should, therefore, be composed of long and flexible molecules of high molecular mass, should be amorphous in their stable unstretched state with a glass transition temperature much lower than the ambient temperature, and finally, should have a network structure to avoid viscous flow of chains.[1] In some cases (thermoplastic elastomers), the presence of a small level of crystallinity ensures the formation of the elastomeric network, because the small crystalline domains act as physical cross-links.

Unusual elastic behavior has also been observed in highly crystalline polymers, such as syndiotactic polypropylene (sPP),[2,3] and some polyesters, such as poly(tetramethylene terephthalate) and poly(trimethylene terephthalate),[4,5] that do not comply with the general requirements described above. This suggests that the elasticity of highly crystalline polymers is compatible only when the crystals actively participate in the elastic recovery of the material. In these cases, and in all crystalline polymers that show unusual elastic properties, both the crystalline and amorphous regions play a key role in determining the mechanical behavior and elasticity. The role of the crystals may show up by the occurrence of either stress-induced phase transitions, as in sPP[2,3] and poly(tetramethylene terephthalate),[4,5] or reversible strains of the crystalline lattice through a continuum of accessible states, as in poly(trimethylene terephthalate).[4,5] The crystals act as cushion for the elastomeric network, storing the mechanical energy applied during the deformation and releasing the energy upon removal of the strain.

The active role of crystals in defining the elastomeric properties of crystalline polymers is discussed in this paper in the case of sPP. It has been recently suggested that polymorphic transformations occurring in the crystalline

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(1) Treolar, L. R. G. *The Physics of Rubber Elasticity*; Claderon Press: Oxford, U.K., 1975.

(2) Auriemma, F.; Ruiz de Ballesteros, O.; De Rosa, C. *Macromolecules* **2001**, *34*, 4485.

(3) Auriemma, F.; De Rosa, C. *J. Am. Chem. Soc.* **2003**, *125*, 13144.

(4) Jakeways, R.; Ward, I. M.; Wilding, M. A.; Hall, I. H.; Desborough, I. J.; Pass, M. G. *J. Polym. Sci., Part B* **1975**, *13*, 799.

(5) Ward, I. M.; Wilding, M. A.; Brody, H. *J. Polym. Sci., Part B* **1976**, *14*, 263.

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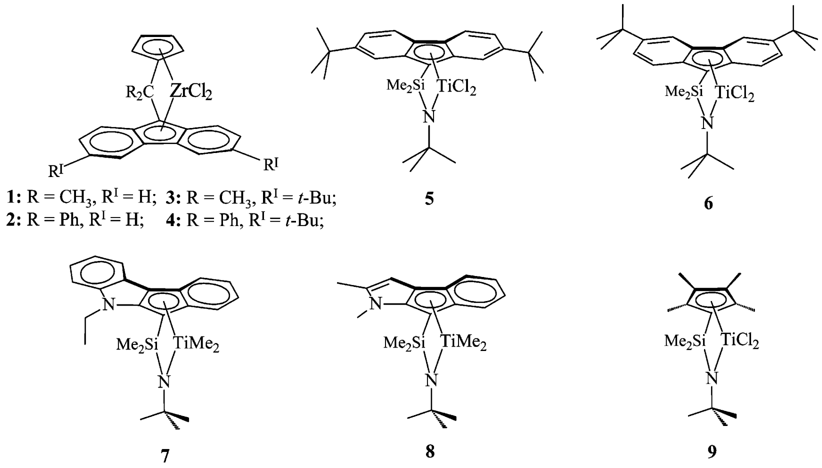
Chart 1. Structure of Zirconocene and Titanocene Complexes Used as Syndiospecific Catalysts of Propene Polymerization



1: R = CH_3, R^I = H; **3:** R = CH_3, R^I = *t*-Bu;
2: R = Ph, R^I = H; **4:** R = Ph, R^I = *t*-Bu;

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phase are in part responsible for elasticity of sPP, and the crystalline domains act, locally, as microscopic engines.[2,3] During elongation, when a given crystal experiences a stress higher than a critical value, a phase transition from the stable helical form into the metastable trans-planar form III occurs[6] and the size of the crystal increases by 38% along the chain axis direction. When the tensile stress is released and a given crystal experiences a stress below a critical value, the trans-planar form III becomes unstable and transforms instantaneously into the more-stable helical form II,[2,3] producing shrinking of the crystals by 38% along the chain axis direction and providing an enthalpic contribution to the elastic recovery. Contemporarily, the return into entropically favored disordered conformations of amorphous chains produces the entropic factor that is also involved in the recovery process. Both the enthalpic factor due to the structural transition in the crystalline regions and the entropic factor due to the conformational transition of the chains in the entangled amorphous phase contemporarily contribute to the elastic recovery of sPP fibers.[2,3]

Because the degree of crystallinity of sPP samples can be easily controlled and modified through the control of the stereoregularity, which, in turn, can be achieved by preparing samples using different metallocene catalysts, sPP provides a unique opportunity for studying the role of crystals in the elasticity.

Depending on the catalyst, it is, indeed, possible to synthesize samples of sPP with different stereoregularities,[7,8] which display different physical properties.[8] Many different catalytic systems have been proposed in the extensive literature on metallocene catalysts.[9−14] The most-important zirconocene and titanocene complexes are shown in the Chart 1. These catalysts produce sPP samples of different stereoregularity, with fully syndiotactic pentad *rrrr* concentrations varying in the wide range 25−96% and melting temperatures varying between 150 and 40 °C.[7,8,10,11]

In this paper, the structure and elastic behavior of sPP samples of different stereoregularity, prepared with the catalysts of Chart 1, are analyzed. We provide a general view of the physical properties of sPP as a function of the degree of stereoregularity and crystallinity. The gradual change in physical properties of sPP with stereoregularity is manifested mainly by the evidence that sPP presents different types of elasticity depending on the degree of crystallinity. We outline the concept that in some semicrystalline polymeric materials, the elasticity may have entropic and enthalpic contributions and crystals may play an active role in the elasticity of crystalline polymers.

Experimental Section

Samples of sPP of different stereoregularity have been prepared with the catalysts of Chart 1. The analyzed samples are listed in Table 1.

Highly stereoregular samples, with fully syndiotactic pentad *rrrr* concentrations in the range 75−96%, have been prepared using the single-center C_s-symmetric metallocene catalyst **1** of Chart 1, isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride ($Me_2C(Cp)(9\text{-}Flu)ZrCl_2$, Me = methyl, Cp = cyclopentadienyl, Flu = fluorenyl), activated with methylaluminoxane (MAO).[9] Samples of different stereoregularity have been obtained with **1**/MAO performing the polymerization at different temperatures (samples sPP1−sPP4, sPP6, sPP7, sPP9, and sPP10 of Table 1).

Highly stereoregular samples with high molecular mass (samples sPP5 and sPP8) have been prepared with catalyst **4** of Chart 1 ($Ph_2C(Cp)(3,6\text{-}t\text{-}Bu_2Flu)ZrCl_2$, Ph = phenyl, *t*-Bu = *tert*-butyl), activated with MAO, at polymerization temperatures of 40 and 60 °C, respectively.[10,11] These two samples have been provided by Dr. A. Razavi of Atofina.

Samples of sPP of medium stereoregularity have been prepared with the constrained geometry catalysts **5** and **6**, described by Razavi et al.[11,14] These Ti complexes, $[Me_2Si(2,7\text{-}t\text{-}Bu_2Flu)(t\text{-}BuN)]$-

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(6) De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5711.
(7) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1997**, *30*, 4137.
(8) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O.; Resconi, L.; Fait, A.; Ciaccia, E.; Camurati, I. *J. Am. Chem. Soc.* **2003**, *125*, 10913.
(9) Ewen, J. A.; Jones, R.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988** *110*, 6255.
(10) Razavi, A.; Bellia, V.; De Brauwer, Y.; Hortmann, K.; Peters, L.; Sirole, S.; Van Belle, S.; Thewalt, U. *Macromol. Chem. Phys.* **2004**, *205*, 347.
(11) Razavi, A.; Bellia, V.; De Brauwer, Y.; Hortmann, K.; Peters, L.; Sirole, S.; Van Belle, S.; Thewalt, U. *Macromol. Symp.* **2004**, *213*, 157.
(12) Grandini, C.; Camurati, I.; Guidotti, S.; Mascellari, N.; Resconi, L.; Nifant'ev, I. E.; Kashulin, I. A.; Ivchenko, P. V.; Mercandelli, P.; Sironi, A. *Organometallics* **2004**, *23*, 344.
(13) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lais, S. Y. (Dow Chemical Company) Eur. Pat. Appl. 0 416 815, 1990.
(14) Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **2001**, *621*, 267.

Table 1. *rrrr* Pentad Concentration, Melting Temperature T_m, and Average Molecular Mass M_w of sPP Samples Prepared with Catalysts of Chart 1

sample	catalyst	[*rrrr*] (%)	T_m (°C)	M_w
sPP1	**1**	95.8	153	266 000
sPP2	**1**	95.0	152	228 000
sPP3	**1**	94.2	149	213 000
sPP4	**1**	92.5	146	164 000
sPP5	**4**	91.5	145	766 000
sPP6	**1**	90.7	140	77 000
sPP7	**1**	88.6	137	115 000
sPP8	**4**	87.0	136	509 000
sPP9	**1**	78.0	124	193 000
sPP10	**1**	74.8	122	52 000
sPP11	**5**	70.6	100	297 000
sPP12	**6**	60.1	77	241 000
sPP13	**7**	54.6	59	1 308 600
sPP14	**8**	51.6	50	672 700
sPP15	**8**	46.9	48	885 700
sPP16	**8**	45.8	48	1 153 200
sPP17	**8**	41.4	45	589 200
sPP18	**9**	26.5		1 190 800

$TiCl_2$ (**5** of Chart 1)[11] and [$Me_2Si(3,6$-*t*-$Bu_2Flu)$(*t*-BuN)]$TiCl_2$ (**6** of Chart 1),[14] give sPP samples characterized by high molecular weight, *rrrr* pentad concentrations in the range 60−80%, and melting temperatures in the range 80−120 °C. Samples sPP11 and sPP12 with *rrrr* contents of 70.6 and 60.1% and prepared with **5** and **6**, respectively, activated with MAO, have been provided by Dr. A. Razavi of Atofina.

Finally, poorly syndiotactic samples with *rrrr* pentad concentrations in the range 40−55% (samples sPP13−sPP17), have been prepared with catalysts **7** and **8**, composed of silyl-bridged indenyl-*tert*-butylamido complexes of titanium, in which the indenyl ligand has a heterocycle condensed onto the cyclopentadienyl moiety.[12] A fully amorphous polypropylene sample (sPP18) with the lowest syndiotacticity ([*rrrr*] = 26%) but very high molecular mass has been prepared with the Dow catalyst dimethylsilyl(tetramethylcyclopentadienyl)(*tert*-butylamido)$TiCl_2$ (catalyst **9** of Chart 1).[13] These samples have been provided by Dr. Luigi Resconi of Basell Polyolefins. All catalysts have been activated with MAO.

The melting temperature, the concentration of the fully syndiotactic *rrrr* pentad, and the average molecular mass of all analyzed samples are reported in Table 1. The melting temperatures were obtained with a Perkin−Elmer DSC-7 differential scanning calorimeter performing scans in a flowing N_2 atmosphere and a heating rate of 10 °C/min. The stereoregularity has been determined by analysis of the ^{13}C NMR spectra.

Unoriented films used for structural analysis and mechanical tests have been obtained by compression molding of as-polymerized samples. Powders of sPP samples have been heated at temperatures 30−40 °C higher than the melting temperatures of the as-prepared samples, between perfectly flat brass plates under a press at very low pressure, kept at these temperatures for 10 min, and slowly cooled to room temperature. Special care has been taken to obtain films with uniform thickness (0.3 mm) and minimal surface roughness, according to the recommendation of the standard ASTM D-2292-85. For samples of low stereoregularity with *rrrr* pentad contents less than 70% (samples sPP11−sPP17), this procedure generally produces amorphous specimens. Crystallization of these amorphous samples has been performed by keeping the compression-molded specimens at room temperature for several days.

Oriented fibers of samples sPP11 and sPP12 have been obtained by stretching compression-molded samples at room-temperature after achieving complete crystallization. Compression-molded films have been kept at room temperature for at least one week before stretching. Stretching has been performed at different values of deformation $\epsilon = 100(L_f - L_0)/L_0$, where L_0 and L_f are the initial and final lengths of the film, respectively. Relaxed fibers have been obtained by keeping the stretched fiber under tension for 2 h and then removing the tension.

X-ray diffraction patterns were obtained with Ni-filtered Cu Kα radiation. The powder profiles were obtained with an automatic Philips diffractometer, whereas the fiber diffraction patters were recorded on a BAS-MS imaging plate (FUJIFILM) using a cylindrical camera and processed with a digital-imaging reader (FUJIBAS 1800). The diffraction patterns have been recorded for stretched fibers soon after the stretching while keeping the fiber under tension, as well as for relaxed fibers, that is, after keeping the fiber under tension for 2 h and then removing the tension, allowing the complete relaxation of the specimens.

Mechanical tests have been performed at room temperature on compression-molded films and oriented fibers with a miniature mechanical tester apparatus (Minimat, by Rheometrics Scientific), following the standard test method for tensile properties of thin plastic sheeting ASTM D882-83. The ratio between the drawing rate and the initial length was fixed equal to 0.1 mm/(mm min) for the measurement of Young's modulus and 10 mm/(mm min) for the measurement of stress−strain curves and the determination of the other mechanical parameters, for instance, the values of the tension set.

Mechanical tests have first been performed on the unstretched compression-molded films. Rectangular specimens 10 mm long, 5 mm wide, and 0.3 mm thick have been stretched up to the break or up to a given strain ϵ. Two benchmarks have been placed on the test specimens and used to measure elongation.

Values of the tension set have been measured on unoriented compression-molded films after breaking according to the standard test method ASTM D412-87. Specimens of initial length L_0 have been stretched up to the break. Ten minutes after breaking, the two pieces of the sample have been fit carefully together so that they are in contact over the full area of the break; the final total length L_r of the specimen has been obtained by measuring the distance between the two benchmarks. The tension set after breaking has been calculated as $t_b = 100(L_r - L_0)/L_0$.

Mechanical cycles of stretching and relaxation have been performed at room temperature on the stress-relaxed fibers and the corresponding hystereses have been recorded. The stress-relaxed fibers have been prepared by stretching compression-molded films of initial length L_0 up to 400 and 600% deformations (final lengths $L_f = 5L_0$ and $7L_0$, respectively), keeping the fibers under tension for 10 min at room temperature and then removing the tension, allowing the specimens to relax to the final length L_r. In the hysteresis cycles, the stress-relaxed fibers with the new initial length L_r have been stretched up to the final lengths $L_f = 5L_0$ or $7L_0$ and then relaxed at controlled rate. After each cycle, the values of the tension set have been measured. The final length of the relaxed specimens L_r' has been measured 10 min after the end of the relaxation step, and the tension set has been calculated as $t_s(\epsilon) = 100(L_r' - L_r)/L_r$.

Results and Discussion

All the studies on the structure and mechanical properties of sPP reported in the literature are in regard to highly syndiotactic samples, with fully syndiotactic *rrrr* pentad concentrations in the range 75−96%,[2,3,7,15−20] and poorly syndiotactic samples, with *rrrr* content in the range 26−55%.[8] These studies have clearly demonstrated that all sPP samples behave as thermoplastic elastomers, regardless of stereoregularity, provided that the molecular mass is high enough. This condition is met in particular for samples prepared with the constrained geometry catalysts **7**−**9** of Chart 1, even though in these cases, poorly syndiotactic and crystalline, or amorphous, samples have been produced, with consequently reduced values of the elastic modulus and mechanical strength.[8] An interesting compromise between properties of poorly syndiotactic samples, with high molecular mass and low elastic modulus,[8] and the highly syndiotactic and crystalline samples, with high elastic modulus but elastic behavior in small deformation ranges,[2,3] can be obtained with sPP samples of medium stereoregularity prepared with constrained geometry catalysts **5** and **6**, described by Razavi et al.[11,14]

The study of the structure and the elastic behavior of sPP samples of medium stereoregularity with *rrrr* pentad concentrations in the range 60−80%, prepared with catalysts **5** and **6**, and the comparison with the mechanical properties of highly stereoregular sPPs, prepared with the C_s-symmetric catalysts **1**−**4**, and the poorly stereoregular samples prepared with catalysts **7**−**9**, may fill the gap between knowledge of the structure and mechanical behavior on highly syndiotactic and crystalline sPPs (with [*rrrr*] = 75−96%) and poorly stereoregular, nearly amorphous samples (with [*rrrr*] = 26−55%).

Samples sPP11 and sPP12 prepared with catalysts **5** and **6**, with syndiotactic pentad *rrrr* concentrations of 70.6 and 60.1%, respectively, do not crystallize by cooling the melt to room temperature. They crystallize if the amorphous samples are kept at room temperature for several days. This behavior is similar to that observed for the poorly syndiotactic samples prepared with catalysts **7** and **8** (samples sPP13−sPP17 of Table 1).[8] The X-ray powder diffraction profiles of samples sPP11 and sPP12 cooled from the melt to room temperature and kept at room temperature for different times up to the complete crystallization are reported in Figure 1.

Both samples crystallize in form I of sPP, as indicated in the X-ray diffraction profiles of Figure 1 by the presence of the 200 and 020 reflections at 2θ = 12.2 and 16°, respectively. The diffraction profiles, however, indicate that disordered modifications of form I are obtained.[7] The absence of the 211 reflection at 2θ = 18.8°, typical of ordered form I,[15] indicates that disorder in the alternation of right- and left-handed helical chains along the axes of the unit cell is present; a broad peak in the range 2θ = 13−19°, centered on the 020 reflection at 2θ = 16°, indicates that a high amount of disorder in the stacking of *bc* layers of chains along *a*, implying shifts of *bc* layers of chains of *b*/4 along *b*, is also present.[7,18] A maximum crystallinity of nearly 25−30% is achieved.

The degree of crystallinity of samples sPP11 and sPP12 is reported in Figure 2 as a function of crystallization time at room temperature in comparison with analogous data for less-stereoregular samples sPP13−sPP17 of Table 1. It is apparent that the crystallization time at room temperature necessary for achieving the maximum crystallinity depends on the stereoregularity and varies from a few hours for the more-syndiotactic samples ([*rrrr*] = 60−70%) to one week for the less-stereoregular samples ([*rrrr*] = 41−55%).

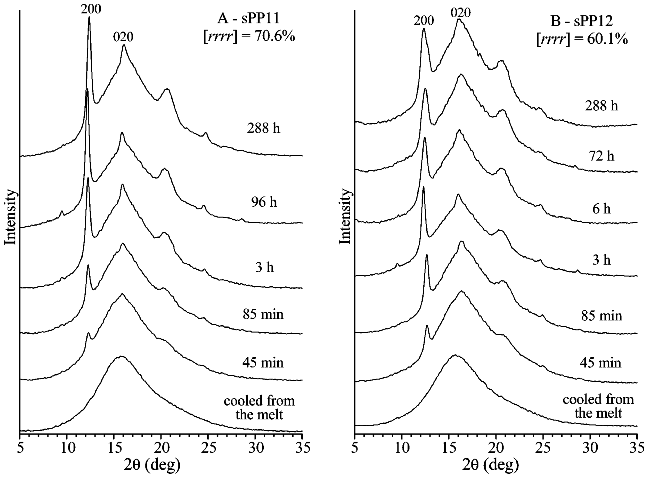

Figure 1. X-ray powder diffraction profiles of samples sPP11 (A) and sPP12 (B) cooled from the melt and kept at room temperature for the indicated time. The 200 and 020 reflections at 2θ = 12 and 16°, respectively, of the helical form I of sPP are indicated.

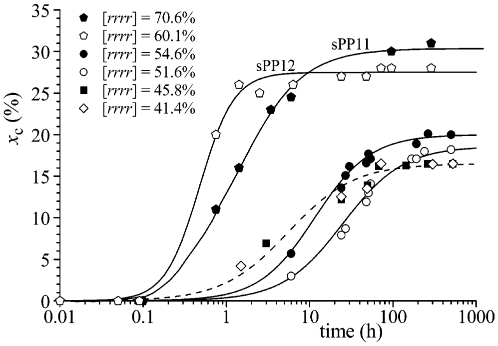

Figure 2. Degree of crystallinity of samples sPP11 (⬟) and sPP12 (⬠) evaluated from the X-ray powder diffraction profiles of Figure 1, as a function of the crystallization time at room temperature in comparison with poorly stereoregular samples sPP13 (●), sPP14 (○), sPP16 (■), and sPP17 (◇) of Table 1.

The stress−strain curves of compression-molded films of samples sPP11 and sPP12 after they have achieved the complete crystallization at room temperature, are reported in Figure 3 in comparison with those of highly stereoregular and crystalline samples, prepared with catalyst **1** of Chart 1 (Figure 3A), and poorly stereoregular samples prepared with catalysts **7** and **8** (Figure 3B).

The values of the mechanical parameters and the degree of crystallinity evaluated from the X-ray diffraction profiles are reported in Table 2. These data show that samples sPP11 and sPP12 of medium stereoregularity ([*rrrr*] = 60−70%) present ductility and toughness at room temperature as high as those of poorly stereoregular samples with [*rrrr*] = 45−55% but higher values of stress at any strain, tensile strength, and Young's modulus, because of the slightly higher crystallinity (about 30% of samples sPP11 and sPP12, against 16−20% of samples sPP13−sPP17, Figure 2). In particular, the values of the tensile strength of samples sPP11 and sPP12

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(15) Lotz, B.; Lovinger, A. J.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.
(16) Lovinger, A. J.; Lotz, B.; Davis, D. D. *Polymer* **1990**, *31*, 2253.
(17) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552
(18) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J. *Macromolecules* **1993**, *26*, 3494.
(19) Chatani, Y.; Maruyama, H.; Noguchi, K.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Part C* **1990**, *28*, 393.
(20) Chatani, Y.; Maruyama, H.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Polym. Phys.* **1991**, *29*, 1649.

Table 2. Values of Elastic Modulus (*E*), Stress (σ_b), Strain (ϵ_b), and Tension Set (t_b) at Break; Stress (σ_y) and Strain (ϵ_y) at the Yield Point; Degree of Crystallinity (x_c) of Compression-Molded Films; and Elastic Modulus of Stress-Relaxed Fibers (E_{Fibers}) of Some sPP Samples of Table 1, Prepared with Catalysts of Chart 1

sample	[*rrrr*] (%)	*E* (MPa)	E_{fibers} (MPa)	σ_b (MPa)	ϵ_b (%)	σ_y (MPa)	ϵ_y (%)	t_b (%)	x_c (%)[a]
sPP3	94.2	256 ± 20	335 ± 20[c]	15 ± 1	400 ± 20	12 ± 1	20 ± 3	300 ± 10	40
sPP5	91.5	146 ± 14		16 ± 4	1000 ± 100	16 ± 1	65 ± 4		45
sPP8	87.0	140 ± 20		20 ± 3	450 ± 15	15 ± 1	47 ± 5		43
sPP9	78.0	119 ± 8	128 ± 2[c], 167 ± 10[d]	12 ± 1	750 ± 20	13 ± 1	44 ± 2	280 ± 10	35
sPP11	70.6	49 ± 6	18 ± 1[d]	16 ± 2	790 ± 40	6.0 ± 0.4	42 ± 4	65 ± 8	31
sPP12	60.1	28 ± 3	17 ± 2[d]	13 ± 1	650 ± 50	5.5 ± 0.5	47 ± 10	30 ± 7	28
sPP13	54.6	19 ± 4	5 ± 1[c]	7 ± 1	650 ± 60	3 ± 1	70 ± 5	59 ± 8	20
sPP14	51.6	14 ± 2	2 ± 1[c]	6 ± 1	530 ± 70	3 ± 1	110 ± 10	48 ± 2	18
sPP15	46.9	4 ± 1	0.54 ± 0.02[c]	4 ± 1	630 ± 80	2.4 ± 0.4	90 ± 10	12 ± 2	16
sPP16	45.8	1.2 ± 0.1	1.0 ± 0.6[c]	3 ± 1	580 ± 70	1.4 ± 0.2	82 ± 7	13 ± 3	16
sPP17	41.4	4 ± 1	1.6 ± 0.3[b]	3.0 ± 0.5	430 ± 60	2.2 ± 0.4	90 ± 6	17 ± 6	16
sPP18	26.5	0.5 ± 0.1	0.1 ± 0.1[c]	1.4 ± 0.1	880 ± 150	1.0 ± 0.1	130 ± 10	21 ± 8	

[a] Evaluated from X-ray powder diffraction profiles. In the case of samples sPP11−sPP17, the compression-molded films were kept at room temperature to allow for complete crystallization of the samples. [b] Elastic modulus of fibers prepared by stretching compression-molded films up to $\epsilon = 200\%$ and then relaxed by removing the tension (stress-relaxed fibers). [c] Elastic modulus of fibers stress-relaxed from $\epsilon = 400\%$. [d] Elastic modulus of fibers stress-relaxed from $\epsilon = 600\%$.

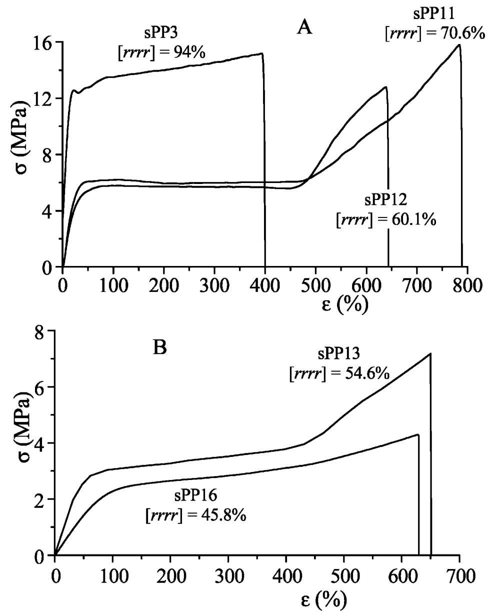

Figure 3. Stress-strain curves of unoriented compression-molded films of samples sPP11 and sPP12 with *rrrr* pentad concentrations of 70.6 and 60.1%, respectively, prepared with catalysts **5** and **6**, compared with the stress−strain curves of highly stereoregular sample sPP3, with an *rrrr* pentad content of 94%, prepared with catalyst **1** (A), and poorly stereoregular and crystalline samples sPP13 and sPP16, having *rrrr* pentad contents of 54.6 and 45.8%, respectively, prepared with catalysts **7** and **8** (B).

are more than twice of those of samples sPP13−sPP17 and very similar to those of highly stereoregular and crystalline samples (Figure 3A), because of the strong strain-hardening occurring at high deformation. The values of the Young modulus for all samples are reported in Table 2 and in Figure 4A as a function of the degree of stereoregularity. The values of Young's modulus of samples sPP11 and sPP12 are about 50 and 30 MPa, respectively, lower than those of highly crystalline samples (256 MPa for sample sPP3)[2] but higher than those of poorly syndiotactic samples sPP13−sPP17 (5−19 MPa).[8]

The values of residual deformation (tension set) after breaking for all samples are reported in Figure 4B as a function of stereoregularity (concentration of *rrrr* pentad). The decrease in the values of the tension set up to nearly 10% with decreasing stereoregularity and crystallinity indicates that elastic recovery after breaking increases with decreasing stereoregularity. This indicates that medium and poorly stereoregular sPP samples show elastic behavior even in the state of unstretched compression-molded films.[8]

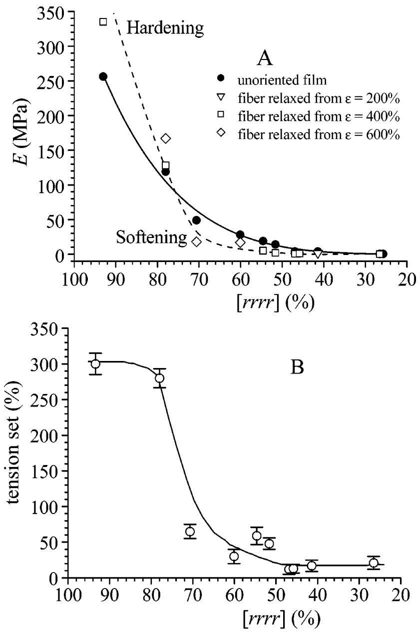

Figure 4. Values of Young's modulus (A) and tension set after breaking (B) of unoriented compression-molded films of sPP samples of different stereoregularity, as a function of the *rrrr* pentad concentration. In A, the Young's modulus of oriented fibers stress-relaxed from 200 (▽), 400 (□), and 600% (◇) deformation are also reported. The stress-relaxed fibers have been prepared by stretching the compression-molded films of initial length L_0 up to 200, 400, and 600% deformations, keeping the fibers under tension for 10 min at room temperature and then removing the tension.

Highly stereoregular and crystalline samples, prepared with catalysts **1**−**4** of Chart 1, instead show large residual deformation after breaking (for instance, for the sample sPP3, a tension set value of 300% has been measured after breaking at 400% deformation) or after deformation at any strain, indicating poor elastic recovery after the first stretching of compression-molded films. This is due to the high crystallinity and the consequently irreversible plastic deformation occurring by stretching bulk isotropic specimens. Samples of medium or very low stereoregularity experience instead a negligible irreversible plastic deformation, because of the

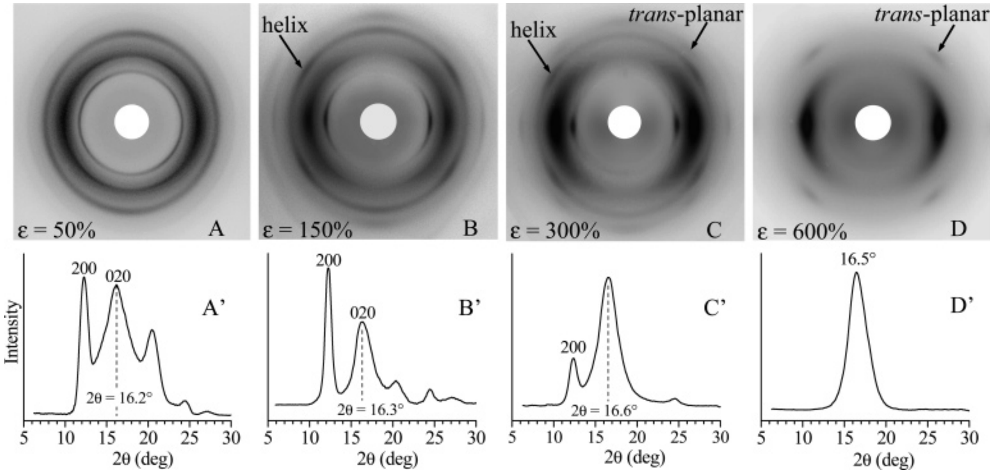

Figure 5. X-ray fiber diffraction patterns (A−D) and corresponding profiles read along the equatorial lines (A′-D′) of fibers of the sample sPP11 with [*rrrr*] = 70.6%, obtained by stretching compression-molded films at room-temperature at values of the strain ϵ of 50 (A), 150 (B), 300 (C), and 600% (D). The 200 and 020 reflections at $2\theta \approx 12$ and 16°, respectively, typical of the helical form I of sPP and the 2θ position of the broad reflection of the mesomorphic form at $2\theta = 16.5°$ are indicated.

very low crystallinity (Table 2), and show a typical behavior of thermoplastic elastomers. The small crystalline domains in the amorphous matrix act as physical knots of the elastomeric lattice, preventing the viscous flow of the amorphous chains. Compared to the poorly stereoregular samples sPP13−sPP17 prepared with catalysts **7** and **8** of Chart 1, which show perfect elastic behavior with low values of strength and modulus, the samples sPP11 and sPP12 of medium stereoregularity that are prepared with catalysts **5** and **6** keep perfect elasticity, even for compression-molded film, which is associated with values of strength similar to those of highly crystalline samples.

The values of Young's modulus of oriented fibers of sPP samples obtained by stretching unoriented films up to a deformation ϵ and then releasing the tension are also reported in Table 2 and in Figure 4A. It is apparent that oriented fibers of highly stereoregular sPP samples, with *rrrr* pentad concentrations higher than 70%, show values of elastic modulus higher than those of the corresponding unoriented films. Moreover, the higher the value of deformation achieved during the stretching of the unoriented film used for preparation of stress-relaxed fibers, the higher the value of the Young's modulus of oriented fibers. Therefore, for highly stereoregular and crystalline samples, stretching and crystal orientation induce hardening of the material (Figure 4A). For sPP samples of lower stereoregularity, with *rrrr* pentad concentrations lower than 60%, the values of the elastic modulus of oriented fibers are lower that those of the corresponding unoriented films; this is probably because of the low level of crystallinity, which is not sufficient to prevent disentanglement of chains in the amorphous network during stretching. In this case, stretching induces a softening of the material (Figure 4A).

These data indicate that it is possible to tailor tacticity, melting temperature, and crystallinity using catalysts of Chart 1 so that sPP samples showing different physical properties of high-modulus thermoplastic materials or soft elastomers can be obtained. Moreover, it is enough to reduce the stereoregularity up to an *rrrr* pentad concentration of nearly 70% to produce thermoplastic elastomers presenting still-high values of strength.

The polymorphic transitions occurring during plastic deformation and successive relaxation have been studied for all samples as a function of stereoregularity by recording the X-ray diffraction patterns during stretching and after releasing the tension.

The X-ray fiber diffraction patterns and corresponding diffraction profiles read along the equatorial line of fiber specimens of the sample sPP11 obtained by stretching compression-molded films at different draw ratios and keeping the fiber under tension are reported in Figure 5.

At low deformations ϵ (up to $\epsilon \approx 150\%$), fibers in helical form I are obtained, as indicated by the presence of the 200 and 020 reflections at $2\theta = 12$ and 16° on the equator (panels A′ and B′ of Figure 5) and reflections on the first-layer line corresponding to the periodicity of the helical conformation (7.4 Å) (panels A and B of Figure 5). With increasing deformation, the intensity of the 200 reflection at $2\theta = 12°$ of the helical form decreases, whereas weak reflections on the first-layer line corresponding to the periodicity of the trans-planar conformation (5.1 Å) appear (panels C and D of Figure 5). At high deformations ($\epsilon = 600\%$), the 200 reflection at $2\theta = 12°$ disappears, and fibers in the trans-planar disordered mesomorphic form are obtained, as indicated by the presence of the broad equatorial reflection in the range $2\theta = 15-18°$ centered at $2\theta = 16.5°$ (Figure 5D).[21] We recall that for poorly syndiotactic samples sPP13−sPP17, the stretching also produces transformation of helical form I into the trans-planar mesomorphic form; the trans-planar form III does not form by stretching,[8] as instead occurs for highly syndiotactic samples.[2,3,6,19] The data of Figure 5 indicate that already for medium values of stereoregularity, starting from an *rrrr* pentad concentration of nearly 70%, the ordered trans-planar form III is destabilized and does not form by stretching. The presence of defects of stereoregularity prevents the formation of form III, probably because these defects are more tolerated in the helical form than in the trans-planar form.[8] The low stereoregularity does not prevent the formation of the trans-planar conformation,

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(21) De Rosa, C.; Ruiz de Ballesteros, O.; Santoro, M.; Auriemma, F. *Macromolecules* **2004**, *37*, 1816.

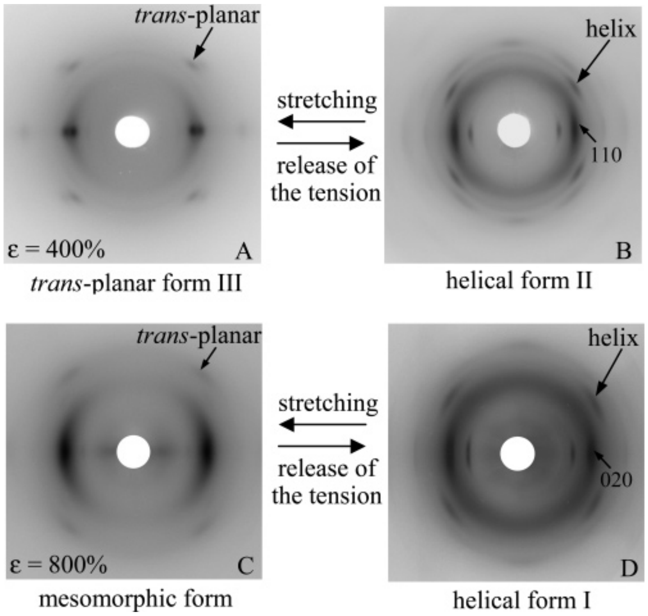

Figure 6. X-ray fiber diffraction patterns of fibers of the highly stereoregular sample sPP3 with [*rrrr*] = 94.2% (A,B) and the sample sPP12 of medium stereoregularity with [*rrrr*] = 60.1% (C,D), stretched at the indicated values of deformation ϵ (A,C) and after the release of the tension (B,D).

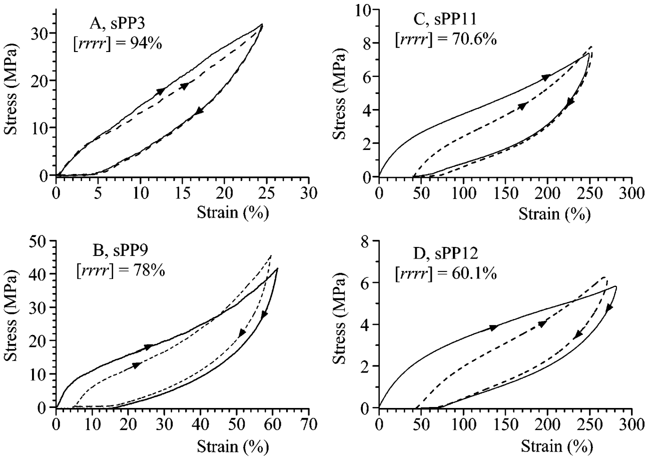

Figure 7. Stress-strain hysteresis cycles of stress-relaxed fibers of the samples sPP3 with [*rrrr*] = 94.2% (A), sPP9 with [*rrrr*] = 78% (B), sPP11 with [*rrrr*] = 70.6% (C), and sPP12 with [*rrrr*] = 60.1% (D). The stress-relaxed fibers have been prepared by stretching compression-molded films of initial length L_0 up to 400 (A) and 600% (B−D) deformations, keeping the fibers under tension for 10 min at room temperature and then removing the tension. In the hysteresis cycles, the stretching steps are performed by stretching the fibers up to the final lengths $L_f = 5L_0$ (A) and $7L_0$ (B−D), where L_0 is the initial length of the unoriented compression-molded films. The first hysteresis cycle (continuous lines) and curves averaged for at least 4 cycles successive to the first one (dashed lines) are reported.

probably because the low crystallinity and the high molecular weight allow for stretching at very high deformation, forming extended chains. However, the high concentration of defects prevents the packing of the trans-planar chains in the ordered lattice of form III, and only the disordered mesomorphic form is obtained (Figure 5).[8]

Diffraction patterns similar to those of Figure 5 have been obtained for the less-stereoregular sample sPP12 ([*rrrr*] = 60.1%), with the only difference being that the critical value of deformation at which the helical form starts transforming into the mesomorphic form is lower than that observed for sample sPP11 and that a pure mesomorphic form can be obtained at values of deformation (800%) higher than that necessary for sample sPP11 (600%, Figure 5D).

The stereoregularity also influences the polymorphic behavior of sPP upon relaxation of fibers by releasing the tension. The X-ray fiber diffraction patterns of fibers of highly stereoregular sample sPP3, with [*rrrr*] = 94%, and sample sPP12 of medium stereoregularity, with [*rrrr*] = 60.1%, stretched at high values of deformation and after the release of the tension, are reported in Figure 6. The trans-planar form III obtained by stretching highly syndiotactic samples (Figure 6A), transforms into isochiral helical form II by releasing the tension,[2,3] as indicated by the presence of the equatorial 110 reflection at $2\theta = 17°$ in the X-ray fiber diffraction pattern of Figure 6B. This polymorphic transition does not occur during relaxation of fibers of less-syndiotactic samples with [*rrrr*] = 45−70%, because in these samples, the trans-planar form III does not form by stretching. In samples of medium and low stereoregularity, the mesomorphic form obtained by stretching (Figure 6C) transforms into helical form I by releasing the tension, as indicated by the presence of the equatorial 020 reflection at $2\theta = 16°$ in the X-ray fiber diffraction pattern of Figure 6D.

A perfect elastic recovery has been observed in successive cycles of stretching and relaxation of the oriented fibers of sPP, regardless of stereoregularity. The hysteresis curves of stress-relaxed fibers of samples sPP11 and sPP12 of medium stereoregularity, with [*rrrr*] = 70.6 and 60.1%, respectively, are reported in Figure 7 in comparison with the hysteresis curves of fibers of samples of higher stereoregularity. The stress-relaxed fibers have been prepared by stretching compression-molded films up to 400 (sample sPP3) and 600% (samples sPP9, sPP11, and sPP12) deformations and then removing the tension. All stress-relaxed fibers of samples of Table 1 show hysteresis curves similar to those of Figure 7, with values of the tension set nearly equal to zero after the cycles successive to the first one.

In the case of highly syndiotactic and crystalline samples, during these mechanical cycles (Figure 7A), a fast reversible crystal−crystal polymorphic transition between helical form II and trans-planar form III occurs (panels A and B of Figure 6). Contrary to the phase transitions occurring in the development of the fibrous morphology starting from the spherulitic morphology, which principally involve destruction of lamellae of helical form I and recrystallization of fibrils of form III, the crystal−crystal polymorphic transition between helical form II and trans-planar form III occurring in fibers does not involve transformation into any intermediate form. This polymorphic transition is in part responsible for the elasticity of highly crystalline sPP due to the enthalpy gain achieved when the fibers are relaxed because the less-stable form III transforms into the more-stable helical form II (panels A and B of Figure 6).[2,3] This enthalpic effect is in addition to the conventional entropic factor due to the conformational transition of the chains in the entangled amorphous phase between random-coil and extended conformations.[2,3]

The enthalpic contribution plays a progressively less important role in the elastic behavior with decreasing stereoregularity and crystallinity. In fact, low syndiotactic and crystalline samples present good elastic properties (panels

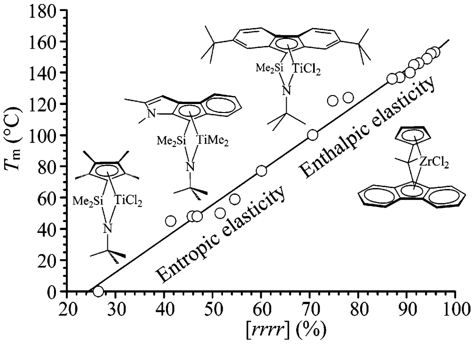

Figure 8. Enthalpic and entropic elasticity of sPP samples with different melting temperatures and crystallinity prepared with different catalysts. Highly syndiotactic samples with high melting temperatures and crystallinity show enthalpic elasticity, whereas samples with low stereoregularity, melting temperatures, and crystallinity exhibit conventional entropic elasticity.

C and D of Figure 7), but the elastic recovery is not associated with the reversible polymorphic transition between trans-planar form III and helical form II (panels C and D of Figure 6). In these samples, the entropic effect of the conformational transition of the amorphous chains between disordered random-coil and extended conformations is mainly responsible for the elasticity.

These data indicate that sPP shows different elastic behaviors depending on the stereoregularity, which can be controlled through the choice of catalysts and the conditions of polymerization. Thermoplastic elastomeric materials based on sPP with finely controlled physical and mechanical properties can be produced. As shown in Figure 8, for the more-stereoregular and crystalline samples with high melting temperatures, prepared with C_s-symmetric catalysts **1**−**4** of Chart 1, the elasticity has a mainly enthalpic character due to the metastability of the trans-planar form III that transforms into the more-stable helical form II during elastic recovery. For less-stereoregular and crystalline samples, with low melting temperatures, or fully amorphous samples, prepared with constrained geometry catalysts **5**−**9** of Chart 1, the elastic recovery is not associated with this polymorphic transition and has a pure entropic origin, as in conventional elastomers. Depending on the melting temperature, elastomers showing conventional entropic or unconventional enthalpic elasticity can be obtained. The development of enthalpic elasticity allows maintenance of elastic properties even when the crystallinity, the melting temperature, and the mechanical strength of the samples are very high. This is possible only thanks to the active role played by crystals in the elastic recovery.

Conclusions

The concept of the active role played by crystals in the elastic behavior of thermoplastic elastomers having a high degree of crystallinity is discussed in the case of syndiotactic polypropylene. This polymer provides an example of a highly crystalline material that shows unconventional elastic properties. Depending on the structure of the metallocene catalysts used for the synthesis, samples of sPP with different-stereoregularity, melting temperature, crystallinity, and physical properties can be produced.

The structure and physical properties of syndiotactic polypropylene of medium stereoregularity prepared with constrained geometry catalysts **5** and **6** of Chart 1 have been studied and compared with those of highly stereoregular samples prepared with C_s-symmetric metallocene catalysts **1**−**4** and poorly syndiotactic, nearly amorphous samples prepared with catalysts **7**−**9**.

These sPP samples of medium stereoregularity show good elastic behavior at room temperature in a large range of deformation. Moreover, these samples present ductility and toughness as high as those of poorly stereoregular samples but much higher strength, similar to that of highly stereoregular and crystalline samples.

Although highly stereoregular and crystalline sPP shows good elastic properties only for oriented fibers, less stereoregular samples present good elasticity even for unoriented compression-molded films during the first stretching. Because of the low crystallinity, these samples experience a negligible irreversible plastic deformation and show a typical behavior of thermoplastic elastomers. The crystalline domains in the amorphous matrix act as physical knots of the elastomeric lattice, preventing the viscous flow of the amorphous chains. The entropic effect of the conformational transition of the amorphous chains, connecting the crystalline domains as tie-chains, is responsible for the elasticity.

The comparison of crystallization and physical properties of sPP of different stereoregularity, variable in a wide range, with *rrrr* pentad content in the range 26−96%, has allowed us to provide a general view of the mechanical behavior of sPP as a function of the degree of stereoregularity and crystallinity. Depending on the catalysts and conditions of polymerization, it is nowadays possible to tailor the tacticity and melting temperature of polypropylene. The control over types and amount of defects, achieved through the choice of the catalyst structure, affords an increased control over the physical properties. The gradual change in physical properties of sPP with stereoregularity is manifested mainly by the evidence that sPPs present different types of elastic behavior depending on the degree of crystallinity. For the most-stereoregular and crystalline samples with high melting temperatures, the elasticity has a mainly enthalpic character due to the metastability of the trans-planar form III that transforms into the more-stable helical form II during elastic recovery. In this case, crystals play an active role in the elastic recovery. For less-crystalline samples, with low melting temperatures, elasticity instead has a pure entropic origin as in conventional thermoplastic elastomers; crystals act only as knots of the physical elastomeric network. The development of enthalpic elasticity allows for maintenance of elastic properties even when the crystallinity, the melting temperature, and the mechanical strength of the samples are very high.

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