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Helical Mesophase of Syndiotactic Polypropylene in Copolymers with 1-Hexene and 1-Octene

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ABSTRACT: Random copolymers of syndiotactic polypropylene (sPP) with hexene and octene comonomeric units have been synthesized in a wide range of comonomer concentrations with a single-center syndiospecific C_s-symmetric metallocene catalyst. The effects of the presence of hexene and octene on the crystallization behavior of sPP and in particular on the stress-induced transformations have been analyzed. All copolymer samples crystallize from the melt in the stable helical form I of sPP. At very low concentrations of hexene or octene (around 1−2 mol %) the behavior of these copolymers is similar to that of sPP; that is, the stable helical form I of the melt-crystallized samples transforms into the *trans*-planar form III by stretching at high deformations. For hexene or octene concentrations in the range 2−5 mol % the stretching produces transformation of the helical form I into the *trans*-planar mesophase. Finally, for hexene or octene concentrations higher than 4−5 mol % the helical form I transforms by stretching at high deformation into a different mesomorphic form, characterized by chains in the ordered 2/1 helical conformation, and disorder in the lateral packing of the chains. This is a first evidence of the crystallization of a solid mesophase of sPP with chains in 2-fold helical conformation, never observed before in the sPP homopolymer.

Introduction

Syndiotactic polypropylene (sPP) crystallizes in a disordered mesomorphic form by quenching the melt to 0 °C and keeping the sample at 0 °C for a long time.[1−15] Samples kept for short time at 0 °C crystallize at room temperature in the more stable helical form I, whereas longer residences at 0 °C favor the mesomorphic form and inhibit the normal crystallization into the helical form I when the sample is heated to room temperature.[1−7] The mesomorphic form transforms into the stable form I of sPP with chains in the 2-fold helical conformation by annealing at 90 °C.[7] Moreover, samples in the mesomorphic form transform into the crystalline form III of sPP with chains in the *trans*-planar conformation by stretching at high deformations.[10−13] However, oriented fibers of sPP in the mesomorphic form have been obtained by stretching films in the mesomorphic form and, then, removing the tension.[10,13] In fact, the crystalline *trans*-planar form III of sPP, obtained by stretching, transforms back into the mesomorphic form by releasing the tension.[13] This transformation is reversible upon successive stretching and relaxing of the fiber, indicating a memory effect of the stress-induced phase transformation.[10] The X-ray fiber diffraction pattern of the mesomorphic form is characterized by broad reflections on the equator at $2\theta = 17°$ and on the first layer line at $2\theta = 24°$, indicating disorder in the structure. The layering of the reflection in the X-ray fiber diffraction pattern, corresponding to a chain periodicity of 5.1 Å, has indicated that the chains in the mesomorphic form are in the ordered *trans*-planar conformation.[1−13] This result has been confirmed by the solid-state ^{13}C NMR spectrum of the quenched sample of sPP in the mesomorphic form,[7] which shows the characteristic resonance of the methylene carbon atoms at $\delta \approx 50$ ppm in the conformational environment TT.TT that indicates an ordered *trans*-planar conformation of the chains.

According to the X-ray diffraction pattern, this solid mesophase is characterized by lateral disorder in the packing of *trans*-planar chains probably associated with a rotational disorder of chains around the chain axes and to translational disorder along the chain axes. Because of these types of disorder, it has been suggested that the *trans*-planar chains of sPP in the mesomorphic aggregates assume locally on average a pseudohexagonal arrangement with $a = 6.02$ Å,[13] which can also be described with an orthorhombic unit cell, reminiscent of the orthorhombic lattice of the ordered form III, with $b = a\sqrt{3} = 10.42$ Å.[13]

The crystallization of the *trans*-planar mesomorphic form of sPP depends on the stereoregularity of the polymer sample.[8] The higher the degree of stereoregularity of the sample, the shorter the permanence time at 0 °C necessary to stabilize the *trans*-planar mesomorphic form and to inhibit the crystallization of the helical form I at room temperature.[8] For stereoirregular sPP samples the pure *trans*-planar mesomorphic form is never obtained even for long permanence time at 0 °C, and the crystallization of the stable helical form is not inhibited.[8] The stereoregularity also influences the structural transformations of the stable helical form I sPP during stretching and involving the formation of the ordered crystalline form III and the mesomorphic form, both characterized by chains in *trans*-planar conformation.[15] In highly syndiotactic samples the helical form I transforms at high deformations into the ordered *trans*-planar form III,[22] whereas in low stereoregular samples[15,23] the high concentration of stereodefects prevents the formation of the crystalline *trans*-planar form III by stretching, and only the disordered mesomorphic form is obtained at high deformations.[23] The mesomorphic form transforms back into the helical form I by releasing the tension.[15,23]

The presence of constitutional defects, as comonomeric units, also affects the polymorphic behavior of sPP and, in particular,

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Table 1. Composition, Melting Temperature of As-Prepared Samples (T_m), Intrinsic Viscosity ([η]), and Viscosity Average Molecular Mass (M_v) of sPPHe and sPPOc Copolymers[a]

samples	comonomer	gas composition (mol % of comonomer)	copolymer composition (mol % of comonomer)[b]	T_m (°C)[c]	[η] (dL/g)[d]	M_v[e]
sPPHe1	1-hexene	1.0	1.7	135.8	3.0	4.1×10^5
sPPHe2	1-hexene	2.0	3.0	125.2	3.75	5.1×10^5
sPPHe3	1-hexene	3.0	3.9	111.3	2.3	3.1×10^5
sPPHe4	1-hexene	4.0	5.6	99.8	3.0	4.1×10^5
sPPHe5	1-hexene	6.0	6.4	83.2	2.7	3.6×10^5
sPPHe6	1-hexene	7.8	9.0	68.3	2.4	3.2×10^5
sPPHe7	1-hexene	9.8	11.2	59.0	2.3	3.1×10^5
sPPHe8	1-hexene	12.0	18.8	53.6	2.6	3.5×10^5
sPPOc1	1-octene	1.25	1.9	134.4	2.4	3.2×10^5
sPPOc2	1-octene	2.5	2.7	124.6	2.4	3.2×10^5
sPPOc3	1-octene	3.75	3.1	111.6	2.0	2.5×10^5
sPPOc4	1-octene	5.0	4.0	104.9	2.1	2.6×10^5
sPPOc5	1-octene	6.25	5.0	99.0	2.4	3.2×10^5
sPPOc6	1-octene	7.5	6.1	92.3	2.4	3.2×10^5
sPPOc7	1-octene	10	9.3	61.1	1.2	1.6×10^5
sPPOc8	1-octene	12.5	18.8	60.0	2.2	2.7×10^5
sPPOc9	1-octene	15	26.1	57.5	2.1	2.6×10^5

[a] Polymerization temperature = 10 °C; pressure = 2 atm; solvent = toluene (140 mL); molar ratio Al/Zr = 1000; catalyst amount = 3 mg; reactor volume = 250 mL; polymerization time = 1 h; yield = 2−4 g. [b] Determined from ^{13}C NMR spectra. [c] Determined from DSC curves of as-prepared samples recorded at heating rate of 10 °C/min. [d] Measured in 1,2,3,4-tetrahydronaphthalene solutions at 135 °C. [e] Molecular masses evaluated from values of intrinsic viscosity.

the stress-induced transformations. The effect of the presence of comonomeric units on the polymorphic behavior of sPP has been extensively investigated in syndiotactic copolymers of propene with ethylene,[24,25] butene,[24,25a,26] pentene,[24] hexene,[24,27,28] 4-methyl-1-pentene,[24,27] octene,[27−32] decene,[27] dodecene,[33] and octadecene.[28] In particular, studies of the stress-induced transformations and of the effect of the presence of comonomers on the stability of helical and *trans*-planar forms of sPP have been reported for copolymers with ethylene[25d−f] and butene.[26e−g]

The presence of ethylene comonomeric units, partially included in the crystals of sPP, increases the relative stability of the polymorphic forms of sPP with chains in *trans*-planar conformation, that is, the form III in fibers of copolymer samples with ethylene contents in the range 2−10 mol % and of the mesomorphic form for ethylene concentrations in the range 10−18 mol %.[25e] For copolymer samples with low ethylene contents, in the range 2−7 mol %, crystals of the helical form I, present in the melt-crystallized samples, transform into the *trans*-planar form III by stretching at high deformations. For copolymers with ethylene content in the range 13−18 mol % the helical form transforms into the *trans*-planar mesomorphic form by stretching.[25e] Even though high concentrations of ethylene units stabilize the *trans*-planar conformation of the chains, the high content of defects prevents the ordered packing of conformationally ordered *trans*-planar chains and, hence, the formation of the ordered crystalline *trans*-planar form III by stretching and the mesophase crystallize at high deformations.[25e]

In the case of propylene-butene (sPPBu) copolymers the presence of butene comonomeric units, also included in crystals of sPP, stabilizes the polymorphic forms of sPP with chains in the helical conformation and fibers in the *trans*-planar mesomorphic form have never been obtained.[26f] The stable helical form I of the melt-crystallized samples transforms into the *trans*-planar form III by stretching only in sPPBu samples with butene content lower than 20 mol %. The presence of butene for concentration higher than 20 mol % prevents the formation of the *trans*-planar form III even by stretching at high degrees of deformation, close to the breaking of the sample, and only fibers in the helical form I are obtained by stretching.[26f,h]

In this paper we present a characterization of copolymers of sPP with 1-hexene and 1-octene. The effect of the presence of 1-hexene and 1-octene comonomeric units on the stability of helical and *trans*-planar forms of sPP and on polymorphic transitions occurring during stretching have been investigated. We show that in these copolymers a different mesomorphic form of sPP, characterized by chains in the 2-fold helical conformation, crystallizes in fiber stretched at high deformations.

Experimental Section

Samples of propylene−hexene (sPPHe) and propylene−octene (sPPOc) syndiotactic copolymers were synthesized with the C_s-symmetric syndiospecific catalyst (phenyl)$_2$methylen(cyclopentadienyl)(9-fluorenyl)zirconium dichloride activated with methylaluminoxane (MAO).

All copolymerizations were run at 10 °C in a 250 mL Pyrex reactor, agitated with magnetic stirrer, containing toluene (100 mL), MAO (5 mL), and liquid 1-hexene or 1-octene. All procedures were conducted in an argon atmosphere, and the residual inert gas was removed up to a final vacuum pressure of 15 mbar. Propene was bubbled through the liquid phase at pressure of 2 bar. The polymerization was started by syringing into the reactor a toluene solution of the catalyst (3 mg), and the Al/Zr molar ratio was maintained at about 1000. The polymerization was stopped when the propene pressure decreases at 1.8 bar. Under such conditions, total monomer conversions were lower than 10%, ensuring a nearly constant feeding ratio. The copolymers were coagulated with excess methanol acidified with enough HCl(aq, conc) to prevent the precipitation of alumina from MAO hydrolysis, filtered, washed with further methanol, and vacuum-dried. Typical yields were 2−3 g. In this condition of polymerization the used catalyst is highly syndiospecific and regioselective (the amount of regioirregularities due to 2,1 insertions of propylene units being less than 0.1%)[15] and allows achieving higher molecular masses for sPP homopolymer and corresponding copolymers. All samples show narrow molecular weight distributions, with M_w/M_n = 2−3, typical of single-center metallocene catalysts. All the synthesized copolymer samples are listed in Table 1.

The compositions of all samples have been obtained from ^{13}C NMR analysis. All spectra were obtained using a Varian XL-200 spectrometer operating in the Fourier transform mode at 120 °C at 50.3 MHz. The samples were dissolved with a 8% w/v concentration in 1,1,2,2-tetrachloroethane-d_2 at 120 °C (also used as internal standard). The peak of the propylene methine carbon atoms was used as internal reference at 28.83 ppm. The resonances in the spectra of sPPHe and sPPOc copolymers were assigned according to ref 34, and the 1-hexene or 1-octene concentrations in the copolymers were determined from the constitutional diads

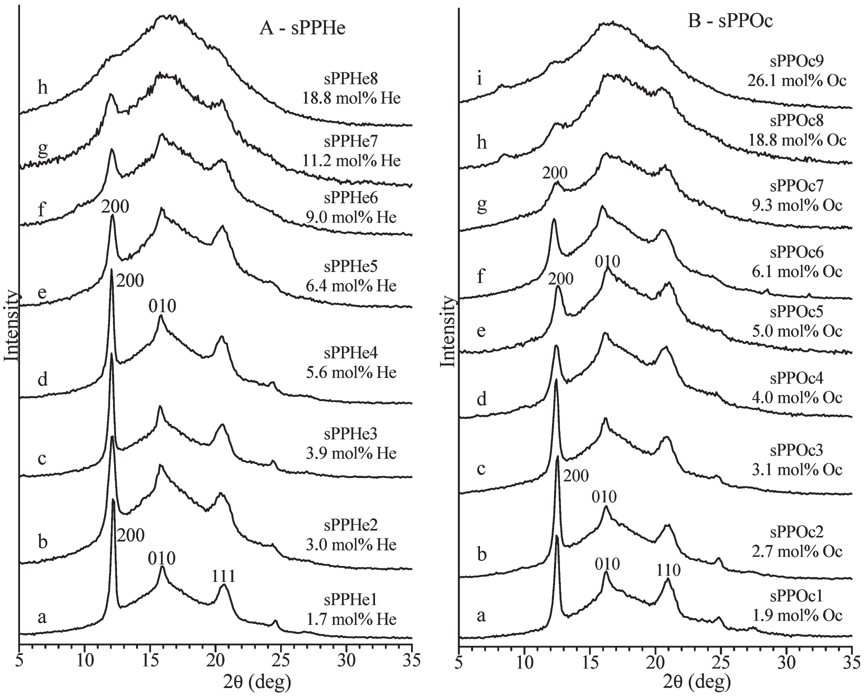

Figure 1. X-ray powder diffraction profiles of compression-molded films slowly crystallized from the melt of sPPHe (A) and sPPOc (B) copolymer samples of the indicated concentration of hexene (He) or octene (Oc). The 200 and 010 reflections of form I of sPP at $2\theta = 12°$ and 16°, respectively, are indicated. For the samples sPPHe6−sPPHe8 with hexene concentration higher than 9 mol %, and the samples sPPOc4−sPPOc9 with octene content higher than 4 mol %, the diffraction profiles of the samples crystallized by aging the amorphous samples at room temperature are reported.

PP, PX, XX distribution (P = propene, X = hexene or octene) using the resonances of the methine and methylene carbon atoms. The NMR data also indicate that all copolymer samples have a random distribution of comonomers and homogeneous intermolecular composition.

The intrinsic viscosities were measured in 1,2,3,4-tetrahydronaphthalene solutions at 135 °C, using a standard Ubbelohde viscosimeter. The viscosity-average molecular masses were obtained from values of intrinsic viscosity using the parameters of the Mark−Houwink equation reported for atactic polypropylene, $\alpha = 0.96$ and $k = 1.24 \times 10^{-5}$ dL/g.[35]

The calorimetric measurements were performed with a differential scanning calorimeter (DSC) Mettler DSC-30 in a flowing N_2 atmosphere.

Films used for the X-ray fiber diffraction characterization have been prepared by compression-molding. Powder samples have been heated at temperatures higher than the melting temperatures under a press at low pressure and slowly cooled to room temperature. Oriented fibers of the copolymer samples have been obtained by stretching at room temperature compression-molded films. Rectangular specimens 10 mm long, 5 mm wide, and 0.3 mm thick have been stretched using a miniature mechanical tester apparatus (Minimat, by Rheometrics Scientific) up to different degrees of deformation $\varepsilon = [(L_f - L_0)/L_0] \times 100$, where L_0 and L_f are the initial and final lengths of the specimen, respectively. Two benchmarks have been placed on the test specimens and used to measure elongation.

X-ray diffraction patterns have been obtained with Ni-filtered Cu Kα radiation. The powder profiles were obtained with an automatic Philips diffractometer, whereas the fiber diffraction patterns were recorded on a BAS-MS imaging plate (FUJIFILM) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800). The X-ray fiber diffraction patterns have been recorded for stretched fibers soon after the stretching while keeping the fiber under tension.

Results and Discussion

The X-ray powder diffraction profiles of compression-molded samples slowly cooled from the melt of sPPHe and sPPOc samples are shown in parts A and B of Figure 1, respectively. sPPHe and sPPOc copolymers with comonomer concentration up to 18.8 and 26.1 mol %, respectively, are crystallized in the helical form I of sPP, as indicated by the presence of the 200 and 010 reflections at $2\theta = 12°$ and 16°, respectively, of form I,[16] in the diffraction profiles of Figure 1. The absence in all the diffraction profiles of the 211 reflection at $2\theta = 18.8°$, typical of the ordered fully antichiral form I of sPP with perfect alternation of right- and left-handed helical chains along both axes of the orthorhombic unit cells,[16−20] indicates that all samples are crystallized in modifications close to the fully disordered form I with disorder in the positioning of right- and left-handed helical chains in the orthorhombic lattice.[15] The Bragg distances of 200 and 010 reflections are basically constant at the values of form I of the sPP homopolymer in all copolymer samples regardless of the comonomer concentration, indicating that hexene and octene units are mainly excluded from crystals of sPP. The crystallinity decreases with increasing comonomer concentrations, and for hexene or octene contents higher than 18−20 mol % the samples are basically amorphous with traces of crystals of form I. The samples sPPHe6−sPPHe8 with hexene concentration higher than 9 mol % and the samples sPPOc4−sPPOc9 with octene content higher than 4 mol % are amorphous soon after the cooling from the melt of the compression-molded samples and slowly crystallize in several days by aging at room temperature. For these samples the diffraction profiles of the fully crystallized aged samples are reported.

The X-ray fiber diffraction patterns, and the corresponding profiles read along the equatorial line, of fibers of the iPPHe and iPPOc copolymers stretched at different deformations are reported in Figures 2 and 3, respectively. For samples with low comonomer concentrations, around 1−3 mol %, both sPPHe and sPPOc copolymers show under stretching a behavior similar to that of the sPP homopolymer.[15] The disordered modifications similar to the B-centered form I of sPP with chains in helical conformation, initially present in the unoriented film (profiles a of Figure 1A,B), transform by stretching at high deformations (ε = 400−500%) into the crystalline form III with chains in *trans*-planar

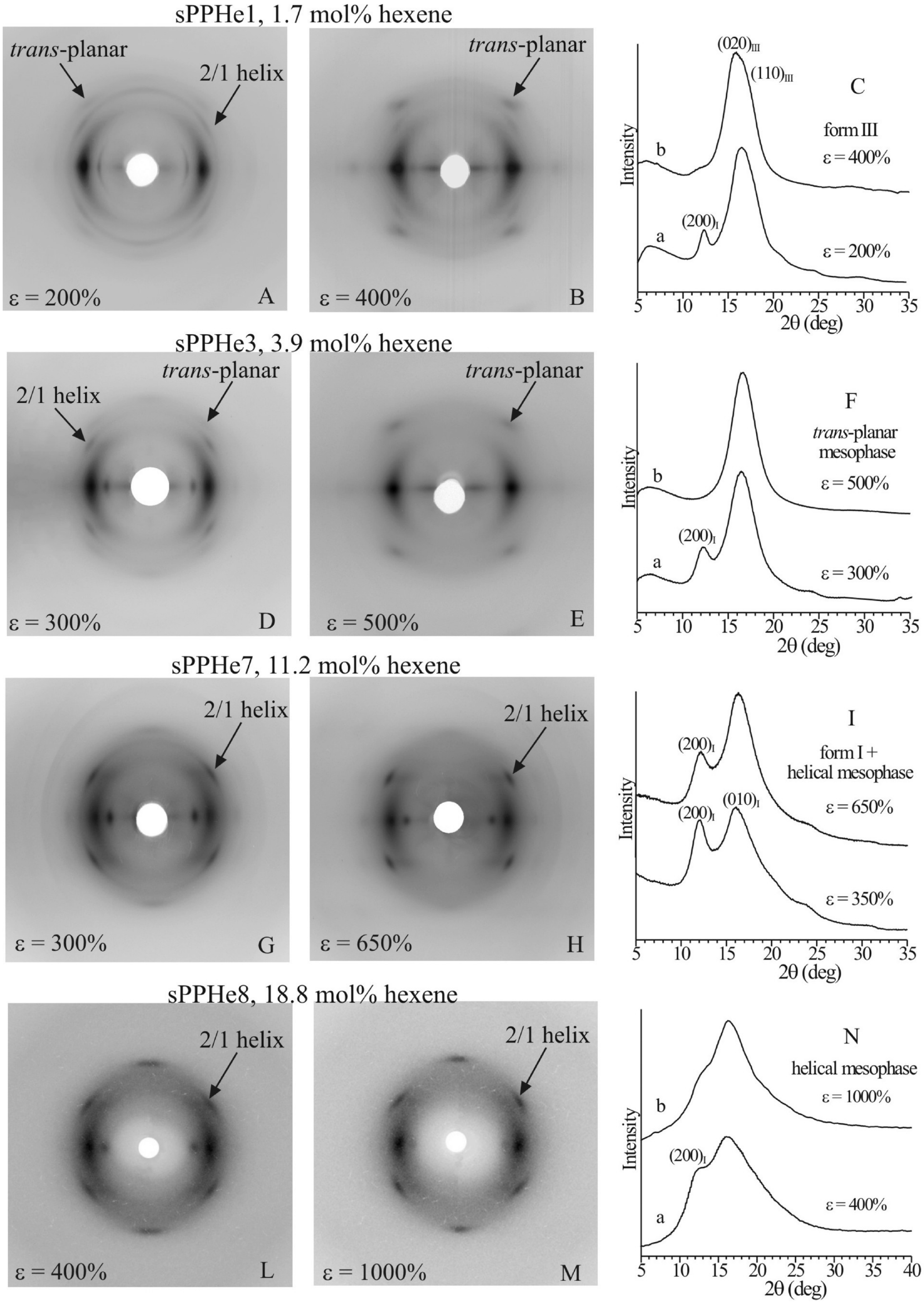

Figure 2. X-ray fiber diffraction patterns and corresponding diffraction profiles read along the equator (C, F, I, N) of fibers of the copolymer samples sPPHe of the indicated hexene concentrations obtained by stretching compression-molded films at the indicated values of the deformation ε. The $(200)_I$ and $(010)_I$ reflections of form I of sPP at $2\theta = 12°$ and 16°, respectively, and the $(020)_{III}$ and $(110)_{III}$ reflections of form III of sPP at $2\theta \approx 16°$ and 18° are indicated.

conformation. (Figures 2A,B and 3A,B). This is indicated in Figures 2A,B and 3A,B for the samples sPPHe1 with 1.7 mol % of hexene and sPPOc1 with 1.9 mol % of octene, respectively, by the low intensity of the $(200)_I$ reflection at $2\theta = 12°$ of the helical form I of sPP (subscript I standing for form I of sPP) (Figures 2C and 3C), the decrease of the intensity of the $(111)_I$ reflection at $2\theta = 20.6°$ on the first layer line corresponding to the chain periodicity of 7.4 Å of the 2/1 helical conformation[15] and the strong intensities of the equatorial $(020)_{III}$ and $(110)_{III}$ reflections at $2\theta \approx 16°$ and 18° of form III of sPP[15,22] (subscript III standing for form III of sPP) (Figures 2C and 3C) and of the $(021)_{III}$ and $(111)_{III}$ reflections on the first layer line, corresponding to the chain periodicity of 5.1 Å of the *trans*-planar conformation.[22] The intensity of the reflections of form I decreases with increasing deformation, and at the highest deformation (400% for sPPHe1.7 and 500% for sPPOc1.9) the oriented fibers appears completely crystallized in the *trans*-planar form III (Figures 2B and 3B).

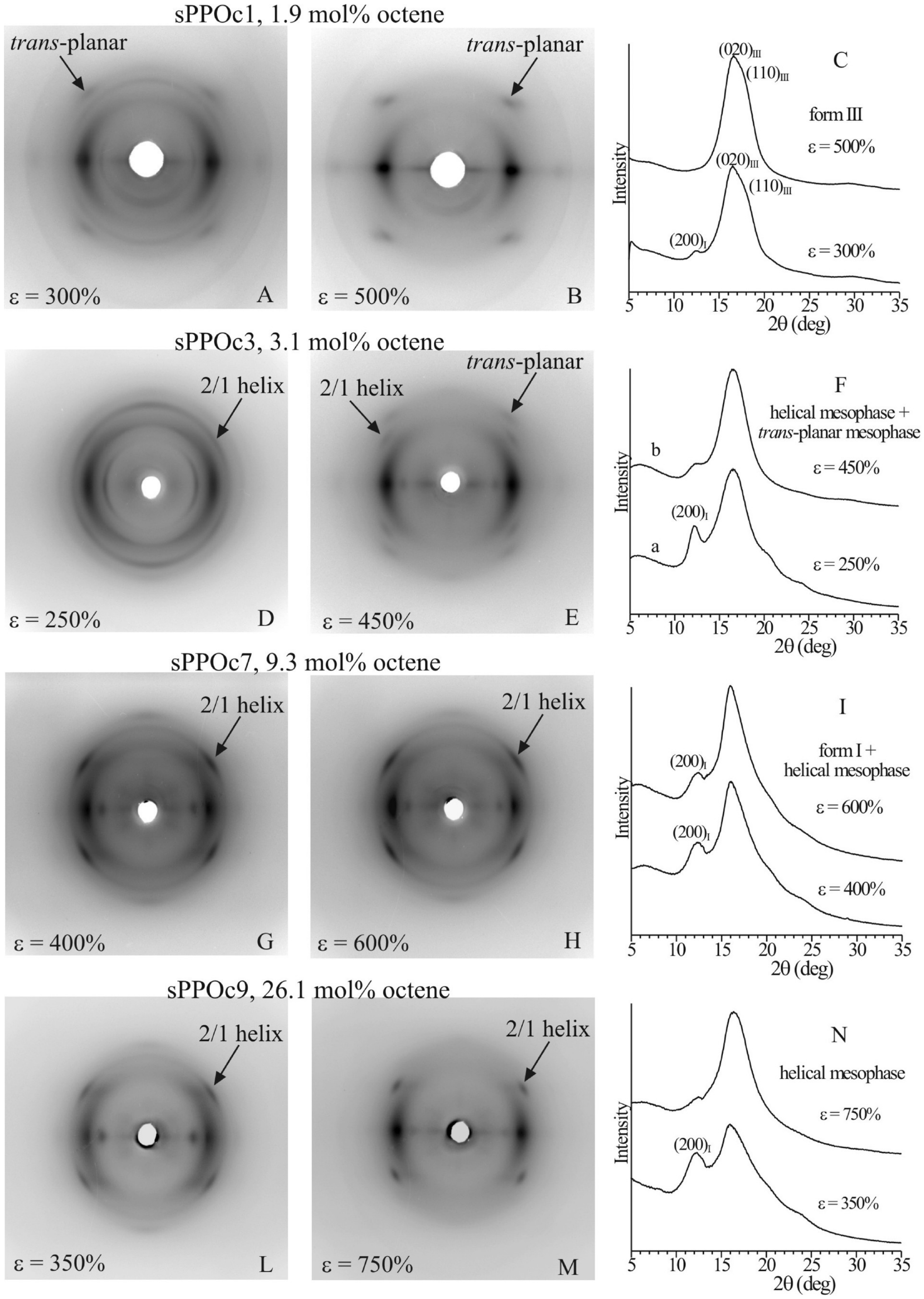

Figure 3. X-ray fiber diffraction patterns and corresponding diffraction profiles read along the equator (C, F, I, N) of fibers of the copolymer samples sPPOc of the indicated octene concentrations obtained by stretching compression-molded films at the indicated values of the deformation ε. The $(200)_{\mathrm{I}}$ reflection of form I of sPP at $2\theta = 12°$ and the $(020)_{\mathrm{III}}$ and $(110)_{\mathrm{III}}$ reflections of form III of sPP at $2\theta \approx 16°$ and 18° are indicated.

Before the complete transformation of form I into form III, the *trans*-planar mesomorphic form is observed in fibers stretched at low degrees of deformation. For example, in the case of the sample sPPHe1 with 1.7 mol % of hexene stretched at 200% deformation a broad halo at $2\theta = 17°$ is present on the equator of the pattern of Figure 2A, and the two $(020)_{\mathrm{III}}$ and $(110)_{\mathrm{III}}$ reflections at $2\theta \approx 16°$ and 18° of form III are not yet developed, while the reflection on the first layer line corresponding to the *trans*-planar conformation is already visible and the reflections of the helical form I are still present on the equator ($(200)_{\mathrm{I}}$ reflection at $2\theta = 12°$) and on the first layer line (Figure 2A and profile a of Figure 2C). This indicates that in sPPHe and sPPOc copolymers with low comonomer concentrations the helical form I transforms in part at low deformations into the *trans*-planar mesomorphic form and then at high deformations into the *trans*-planar form III. The same behavior has been observed for the samples sPPHe2 and sPPOc2 containing about 3 mol % of hexene or octene.

With increasing hexene or octene concentrations a progressive destabilization of the crystalline form III of sPP with chains in the *trans*-planar conformation is observed. In fact, already in the samples sPPHe3 with 3.9 mol % of hexene and sPPOc3 with 3.1 mol % of octene, the *trans*-planar form III does not form by stretching even at the maximum deformation (Figures 2D−F and 3D−F) and is no longer observed in the fibers of samples with higher comonomer concentrations. However, in the samples sPPHe3 and sPPOc3 the helical form I present in the unstretched films (Figure 1) transform by stretching in the *trans*-planar mesomorphic form of sPP, as indicated by the decrease of the intensity of the $(200)_{\mathrm{I}}$ reflection of form I and the presence of the broad halo at $2\theta = 17°$, typical of the *trans*-planar mesomorphic form, on the equator of the diffraction patterns of Figures 2D,E and 3D,E, and of the reflection on the first layer line corresponding to the *trans*-planar conformation. At the maximum deformation fibers in the pure *trans*-planar mesomorphic form are obtained for the sample sPPHe3, as indicated by the absence of any reflections of the helical form I in the diffraction pattern of Figure 2E, whereas for the sample sPPOct3, at nearly the same comonomer concentration, stretched at the maximum deformation, the *trans*-planar mesomorphic form is in mixture with residual crystals of the helical form I, as indicated by the presence of the $(200)_{\mathrm{I}}$ reflection of form I with very low intensity and of reflections on the first layer line corresponding to both helical and *trans*-planar conformations in the diffraction pattern of Figure 3E. These data indicate that the presence of hexene or octene comonomeric units at concentrations around 3−4 mol % prevents the crystallization of the *trans*-planar form III. The bulky hexene or octene side groups destabilize the *trans*-planar conformation of the chains of sPP;[15] however, at these concentrations long stretches of the copolymer chains may still assume the *trans*-planar conformation in the stretched fibers, but the high degree of disorder due to the presence of the bulky side groups of hexene or octene counits prevents the crystallization of these portions of chains in *trans*-planar conformation in the ordered crystalline form III, and only the disordered *trans*-planar mesomorphic form is obtained.

With further increase of hexene or octene concentration the *trans*-planar conformation becomes much less stable than the 2-fold helical conformation, and in stretched fibers of sPPHe and sPPOc copolymers with hexene or octene contents higher than 5−6 mol % also the disordered *trans*-planar mesomorphic form does not form even at high deformations. The X-ray fiber diffraction patterns of fibers of the samples sPPHe7 with 11.2 mol % of hexene and sPPOc7 with 9.3 mol % of octene are shown in Figures 2G−I and 3G−I. It is apparent that the diffraction patterns of fibers stretched at low and high deformations present only the reflections of the helical form I ($(200)_{\mathrm{I}}$ and $(010)_{\mathrm{I}}$ at $2\theta = 12°$ and 16°, respectively, on the equator and the $(111)_{\mathrm{I}}$ reflection at $2\theta = 20.6°$ on the first layer line),[16] and all the reflections of the *trans*-planar forms (mesophase or form III) are absent.

This would indicate that crystals of form I present in the unstretched film are only oriented during stretching to obtain fibers of form I. However, in both samples sPPHe7 and sPPOct7 the equatorial profiles of Figures 2I and 3I show that the intensity of the $(200)_{\mathrm{I}}$ reflection of the helical form I at $2\theta = 12°$ decreases with increasing deformation and is very low for the sample sPPOct7 stretched at 600% deformation (Figure 3H,I). This suggests that crystals of form I present in the unstretched film undergo some transformation during stretching. Since no reflections of *trans*-planar forms of sPP (mesophase or form III) are visible in the diffraction patterns of Figures 2G,H and 3G,H, the transformation of the helical form into the *trans*-planar form must be excluded. The low intensity of the $(200)_{\mathrm{I}}$ reflection at $2\theta = 12°$ and the contemporary presence in the diffraction patterns of Figures 2H and 3H of the equatorial reflection at $2\theta = 16°$ and of the reflection on the first layer line corresponding to the 2/1 helical conformation, which both have still strong intensities, indicate that crystals with chains in the 2/1 helical conformation, different from the crystalline form I of sPP, are formed in the stretched fibers.

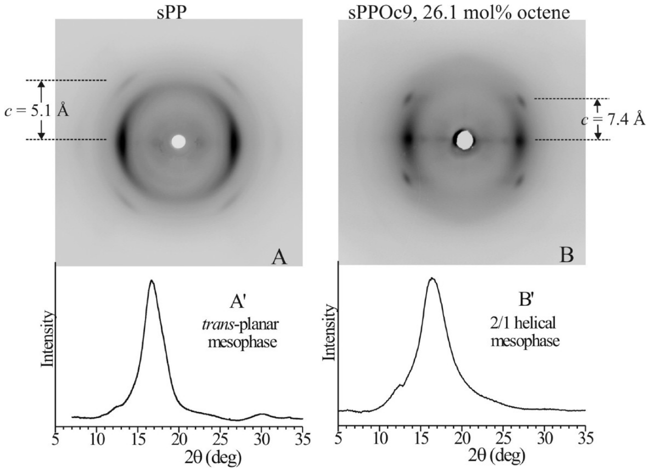

Figure 4. Comparison between the X-ray fiber diffraction patters (A, B) and the corresponding equatorial diffraction profiles (A′, B′) of the *trans*-planar mesophase of sPP (A, A′) obtained by stretching the unoriented sample in the mesomorphic form and then removing the tension[10,13] and of the helical mesophase of sPP (B, B′) obtained in the fibers of the copolymer sample sPPOc9 with 26.1 mol % of octene. The distances between the equator and the first layer line, corresponding to the periodicity of $c = 5.1$ Å of the *trans*-planar conformation of the chains in the mesophase of sPP (A) and a periodicity of $c = 7.4$ Å of the 2/1 helical conformation of the chains in the mesophase of the propylene−octene copolymers (B), are indicated.

This result becomes clear in the copolymer samples sPPHe8 and sPPOc9 with the highest hexene and octene concentrations (18.8 mol % of hexene and 26.1 mol % of octene, respectively). Compression-molded films of these samples are basically amorphous with only a very small amount of crystals of the helical form I, as indicated by the presence of the very low intensity peaks at $2\theta = 12°$, 16°, and 20° in the diffraction profiles h and i of Figures 1A and 1B, respectively. The fiber diffraction patterns of these samples are shown in Figures 2L−N and 3L−N. The stretching of these samples produces further crystallization, and well-oriented crystalline fibers are obtained at high deformations. At low deformations, broad and low-intensity $(200)_{\mathrm{I}}$, $(010)_{\mathrm{I}}$, and $(111)_{\mathrm{I}}$ reflections of form I are clearly present in the diffraction patterns of Figures 2L and 3L, indicating that the stretching produces at the beginning further crystallization of form I. At high deformations, the diffraction patterns of Figures 2M and 3M present a broad strong equatorial reflection at $2\theta = 16°$ and a strong reflection on the first layer line at $2\theta = 20°$, corresponding to the helical conformation, but the $(200)_{\mathrm{I}}$ reflection at $2\theta = 12°$ is practically absent. This indicates that crystals of form I transform at high deformations in a disordered mesomorphic form with chains in the ordered 2/1 helical conformation. This is the first evidence of the crystallization of a solid mesophase of sPP with chains in 2-fold helical conformation, never observed before in the sPP homopolymer. Contrary to butene units that stabilize the helical conformation of sPP chains and induce crystallization of the ordered crystalline helical form I,[26f] high concentrations of hexene or octene units stabilize the helical conformation of the chains, but the high content of constitutional defects prevents the formation of the ordered crystalline form I by stretching and the helical mesophase crystallizes at high deformations.

The diffraction patterns of Figures 2M and 3M indicate that, as in the case of the *trans*-planar mesophase, the helical mesophase is characterized by long-range order in the conformation of

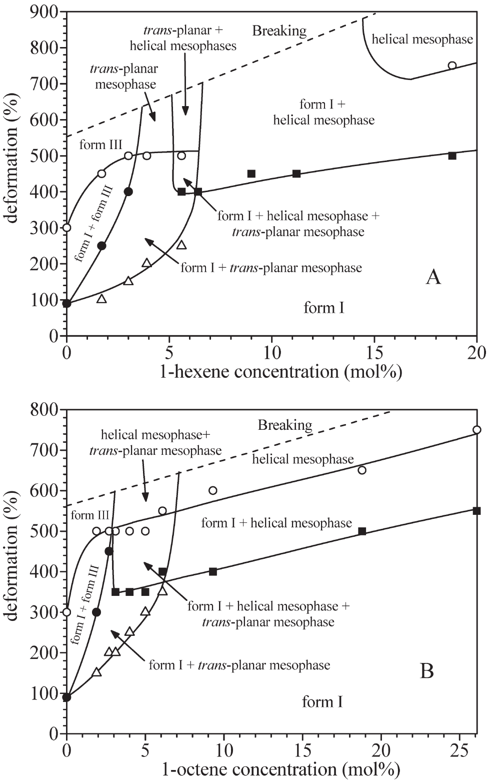

Figure 5. Phase diagram of (A) sPPHe and (B) sPPOc copolymers showing the regions of stability of the different polymorphic forms as a function of strain and copolymer composition.

the chains and high degree of disorder in the lateral packing of the 2/1 helical chains. The presence of a narrow diffraction peak on the first layer line in a position close to the reflection of the helical form I[15,36] indicates that some kind of short-range order is maintained in the helical mesomorphic aggregates, probably consisting in the tendency of first neighboring chains to face each other as in the crystals of the stable helical form I.[16]

The fiber diffraction patterns, and the corresponding equatorial profiles, of the *trans*-planar mesophase of sPP homopolymer and the helical mesophase found in sPPHe and sPPOc copolymers are compared in Figure 4. It is apparent that the diffraction patterns are very similar; they present a very similar equatorial profile with a broad single reflection at $2\theta = 16°-17°$ and a first layer line reflection. The only difference is the separation between layer lines, which corresponds to the periodicity of $c = 5.1$ Å of the *trans*-planar conformation of the chains in the mesophase of sPP (Figure 4A) and a periodicity of $c = 7.4$ Å of the 2/1 helical conformation of the chains in the mesophase of the propylene–hexene and propylene–octene copolymers (Figure 4B).

The data of Figures 2 and 3 have allowed building the phase diagrams of the sPPHe and sPPOc copolymers, shown in Figure 5, where the region of stability of the different polymorphic forms of sPP in oriented fibers are defined as a function of copolymer composition and degree of deformation. The boundary lines in the phase diagrams define the transformations of the helical form I of sPP into the *trans*-planar form III of sPP, at hexene or octene concentrations lower than 3 mol %, in the *trans*-planar-mesomorphic form for hexene or octene concentration in the range 3–6 mol % and in the helical mesophase for higher comonomer concentrations. The boundary lines have been determined by the emergence during deformation of reflections typical of the polymorphic forms of sPP in the X-ray fiber diffraction patterns. The values of the critical strain at which the polymorphic transitions start and at which the transformations are complete depend on type of comonomeric unit and the copolymer composition. Moreover, the width of the regions of stability of the different polymorphic forms are slightly different in sPPHe and sPPOc copolymers. It is apparent, indeed, from Figure 5 that fibers in the pure *trans*-planar mesophase can be obtained only in sPPHe copolymers for hexene concentrations in the range 3–5 mol % (Figure 5A), whereas in sPPOc copolymers the *trans*-planar mesophase is always in mixture with the helical form I, at low degrees of deformation, or with the helical mesophase, at higher deformations (Figure 5B). Furthermore, whereas in sPPHe copolymers the formation of the helical mesophase at high degrees of deformation occurs for hexene concentrations higher than 5 mol % (Figure 5A), in sPPOc copolymers the helical mesophase starts forming already for octene concentrations of 3 mol % (Figure 5B). Finally, the pure helical mesophase can be obtained in sPPHe copolymers only at very high hexene concentrations (around 18 mol %) (Figure 5A), whereas in sPPOc copolymers fibers in the pure helical mesophase can be obtained already for octene concentrations higher than 6–7 mol % (Figure 5B), resulting in a much wider region of stability of the helical mesophase in sPPOc copolymers. These differences reflects the stronger effect of stabilization of the helical conformation and destabilization of the *trans*-planar conformation of sPP chains of octene units compared to hexene units.

Conclusions

Random copolymers of syndiotactic polypropylene with hexene and octene comonomeric units have been synthesized in a wide range of comonomer concentration with a single-center syndiospecific C_s-symmetric metallocene catalyst. The effects of the presence of hexene and octene on the crystallization behavior of sPP and in particular on the stress-induced transformations have been analyzed.

All copolymer samples crystallize from the melt in the stable helical form I of sPP and crystallinty is still present up to a concentration of comonomers of 20–26 mol %. The presence of the branched comonomers, however, influences the polymorphic behavior when the samples are stretched at high deformations. They destabilize the *trans*-planar conformation of sPP chains and at relatively high concentrations (higher than 5–6 mol %) prevents the crystallization of both the *trans*-planar form III and the *trans*-planar mesophase.

At low concentrations of hexene or octene (in the range 1–3 mol %) the behavior of these copolymers is similar to that of sPP; that is, the stable helical form I of the melt-crystallized samples transforms into the *trans*-planar form III by stretching at high deformations. For hexene or octene concentrations in the range 3–5 mol % the stretching produces transformation of the helical form I into the *trans*-planar mesophase. Finally, for hexene and octene concentrations higher than 5–6 and 3 mol %, respectively, the helical form I transforms by stretching at high deformation into a different mesomorphic form, characterized by chains in the ordered 2/1 helical conformation and disorder in the lateral packing of the chains. High concentrations of hexene or octene units stabilize the helical conformation of the chains, but the high content of constitutional defects prevents the formation of the ordered crystalline form I by stretching and the helical mesophase crystallize at high deformations. This is the first evidence of the crystallization of a solid mesophase of sPP with chains in 2-fold helical conformation, never observed before in the sPP homopolymer. These data have allowed building phase diagrams of the long branched copolymers of sPP where the region of stability of the different polymorphic forms of sPP in oriented fibers is defined as a function of copolymer composition and degree of deformation.

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References and Notes

(1) Nakaoki, T.; Ohira, Y.; Hayashi, H.; Horii, F. *Macromolecules* **1998**, *31*, 2705.
(2) Ohira, Y.; Horii, F.; Nakaoki, T. *Macromolecules* **2000**, *33*, 1801.
(3) Nakaoki, T.; Yamanaka, T.; Ohira, Y.; Horii, F. *Macromolecules* **2000**, *33*, 2718.
(4) Ohira, Y.; Horii, F.; Nakaoki, T. *Macromolecules* **2000**, *33*, 5566.
(5) Ohira, Y.; Horii, F.; Nakaoki, T. *Macromolecules* **2001**, *34*, 1655.
(6) Nakaoki, T.; Ohira, Y.; Horii, F. *Polymer* **2001**, *42*, 4555.
(7) Vittoria, V.; Guadagno, L.; Comotti, A.; Simonutti, R.; Auriemma, F.; De Rosa, C. *Macromolecules* **2000**, *33*, 6200.
(8) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O. *Polymer* **2001**, *42*, 9729.
(9) De Rosa, C.; Ruiz de Ballesteros, O.; Santoro, M.; Auriemma, F. *Polymer* **2003**, *44*, 6267.
(10) De Rosa, C.; Ruiz de Ballesteros, O.; Santoro, M.; Auriemma, F. *Macromolecules* **2004**, *37*, 1816.
(11) Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V. *Macromolecules* **2000**, *33*, 6023.
(12) Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V. *Macromolecules* **2001**, *34*, 2512.
(13) Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V.; Meille, S. V. *Macromolecules* **2002**, *35*, 3921.
(14) Grasruck, M.; Strobl, G. *Macromolecules* **2003**, *36*, 86.
(15) De Rosa, C.; Auriemma, F. *Prog. Polym. Sci.* **2006**, *31*, 145.
(16) Lotz, B.; Lovinger, A. J.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.
(17) Lovinger, A. J.; Lotz, B.; Davis, D. D. *Polymer* **1990**, *31*, 2253.
(18) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552.
(19) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J. *Macromolecules* **1993**, *26*, 3494.
(20) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Schumacher, M. *Macromolecules* **1994**, *27*, 6603.
(21) Stocker, W.; Schumacher, M.; Graff, S.; Lang, J.; Wittmann, J. C.; Lovinger, A. J.; Lotz, B. *Macromolecules* **1994**, *27*, 6948.
(22) Chatani, Y.; Maruyama, H.; Noguchi, K.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Part C* **1990**, *28*, 393.
(23) (a) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O. *Chem. Mater.* **2006**, *18*, 3523. (b) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O.; Resconi, L.; Fait, A.; Ciaccia, E.; Camurati, E. *J. Am. Chem. Soc.* **2003**, *125*, 10913. (c) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O. *Macromolecules* **2003**, *36*, 7607. (d) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O. *Macromolecules* **2004**, *37*, 1422.
(24) (a) Kakugo, M. *Macromol. Symp.* **1995**, *89*, 545. (b) Naga, N.; Mizunuma, K.; Sadatoshi, H.; Kakugo, M. *Macromolecules* **1997**, *30*, 2197. (c) Naga, N.; Mizunuma, K.; Sadatoshi, H.; Kakugo, M. *Polymer* **2000**, *41*, 203.
(25) (a) De Rosa, C.; Auriemma, F.; Vinti, V.; Grassi, A.; Galimberti, M. *Polymer* **1998**, *39*, 6219. (b) De Rosa, C.; Auriemma, F.; Talarico, G.; Busico, V.; Caporaso, L.; Capitani, D. *Macromolecules* **2002**, *35*, 1314. (c) De Rosa, C.; Auriemma, F.; Fanelli, E.; Talarico, G.; Capitani, D. *Macromolecules* **2003**, *36*, 1850. (d) De Rosa, C.; Auriemma, F. *Adv. Mater.* **2005**, *17*, 1503. (e) De Rosa, C.; Auriemma, F. *Polymer* **2006**, *47*, 2179. (f) De Rosa, C.; Auriemma, F. *Macromolecules* **2006**, *39*, 249.
(26) (a) De Rosa, C.; Talarico, G.; Caporaso, L.; Auriemma, F.; Fusco, O.; Galimberti, M. *Macromolecules* **1998**, *31*, 9109. (b) De Rosa, C.; Auriemma, F.; Caporaso, L.; Talarico, G.; Capitani, D. *Polymer* **2000**, *41*, 2141. (c) De Rosa, C.; Auriemma, F.; Orlando, I.; Talarico, G.; Caporaso, L. *Macromolecules* **2001**, *34*, 1663. (d) Zhang, B.; Yang, D.; De Rosa, C.; Yan, S. *Macromolecules* **2002**, *35*, 4646. (e) De Rosa, C.; Auriemma, F.; Caliano, L.; Talarico, G.; Corradi, M. *Macromolecules* **2008**, *41*, 5301. (f) De Rosa, C.; Auriemma, F.; Corradi, M.; Caliano, L.; Talarico, G. *Macromolecules* **2008**, *41*, 8712. (g) De Rosa, C.; Auriemma, F.; Caliano, L.; Corradi, M. *Macromol. Mater. Eng.* **2008**, *293*, 810. (h) De Rosa, C.; Auriemma, F.; Corradi, M.; Caliano, L.; Ruiz de Ballesteros, O.; Di Girolamo, R. *Macromolecules* **2009**, *42*, 4728. (i) Jiang, S.; Li, H.; De Rosa, C.; Auriemma, F.; Yan, S. *Macromolecules* **2010**, *43*, 1449.
(27) Schwerdtfeger, E. D.; Miller, S. A. *Macromolecules* **2007**, *40*, 5662.
(28) Arranz-Andrés, J.; Guevara, J. L.; Velilla, T.; Quijada, R.; Benavente, R.; Pérez, E.; Cerrada, M. L. *Polymer* **2005**, *46*, 12287.
(29) Jungling, S.; Mulhaupt, R.; Fisher, D.; Langhauser, F. *Angew. Makromol. Chem.* **1995**, *229*, 93.
(30) Thomann, R.; Kressler, J.; Mulhaupt, R. *Macromol. Chem. Phys.* **1997**, *198*, 1271.
(31) Thomann, R.; Kressler, J.; Mulhaupt, R. *Polymer* **1998**, *39*, 1907.
(32) Hauser, G.; Schmidtke, J.; Strobl, G. *Macromolecules* **1998**, *31*, 6250.
(33) Graef, S. M.; Wahner, U. M.; Van Reenen, A. J.; Brull, R.; Sanderson, R. D.; Pasch, H. *J. Polym. Sci., Part A* **2002**, *40*, 128.
(34) Kissin, Y. V.; Brandolini, A. J. *Macromolecules* **1991**, *24*, 2632.
(35) Brandrup, L.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*; John Wiley: New York, 1999.
(36) De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5711.