Macromolecules **2005,** *38,* 8345−8352 **8345**

Synthesis, Characterization, and Crystalline Structure of Syndiotactic 1,2-Polypentadiene: The Trans Polymer

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Received November 19, 2004; Revised Manuscript Received June 17, 2005

ABSTRACT: (*E*)-1,3-Pentadiene was polymerized with the $CoCl_2(P^iPrPh_2)_2$−MAO system, obtaining a crystalline polymer with a melting point of 168 °C. The polymer was characterized by IR, NMR (^{13}C and ^1H in solution and ^{13}C in the solid-state), DSC, GPC, and X-ray diffraction, and it was found to have a *trans*-1,2 syndiotactic structure. The fiber periodicity of 5.14 ± 0.03 Å indicates a *trans*-planar main-chain conformation similar to the one found in 1,2-syndiotactic polybutadiene. Molecular mechanics calculations using the MM2 force field show that, for *trans*-1,2 syndiotactic polypentadiene (t-12 sPPD), the all-trans main-chain conformation is more stable with respect to the (T_2G_2) arrangement, consistent with structural data of most 1,2-syndiotactic polydienes but at variance with the cis isomer and with 1,2-poly(4-methyl-1,3-pentadiene). The crystalline structure of t-12 sPPD has been determined on the basis of a unit cell derived from fiber data and refined using the Rietveld method on unoriented patterns. Like both 1,2-syndiotactic polybutadiene and 3,4-syndiotactic polyisoprene, it adopts the high-symmetry orthorhombic space group *Pbcm* with the following refined lattice parameters: $a = 6.59(1)$, $b = 14.69(1)$, and c (chain axis) = 5.11(3) Å. The two chains in the unit cell also present, besides crystallographic intramolecular glide planes, intramolecular 2-fold axes and planes of symmetry, both orthogonal to the glide plane. The main-chain conformation is slightly distorted from planarity, while the side chains adopt the same idealized skew arrangement found in other *trans*-1,2 syndiotactic polydienes. The refinement, giving the quality of the available data, is satisfactory. The thermal parameters, the relatively loose packing, and some features of the refined geometry points to disorder in the structure that we were unable to detail further using simple crystallographic models.

Introduction

Polydienes exhibit a much greater variety of isomeric structures than poly-α-olefins: indeed *cis*-1,4, *trans*-1,4, 1,2, or 3,4 diene polymers have been synthesized. Isotactic or syndiotactic isomers can be obtained in the case of *cis*-1,4 and *trans*-1,4 polymers when an asymmetric carbon is present in the polymer chain. Stereoregular 1,2- or 3,4-polydienes may also exhibit iso- or syndiotacticity, and depending on the structure of the monomer polymerized, the double bond in the side chain may present a trans or a cis configuration. As a consequence of this abundance of possible regular structures, polydienes afford unique opportunities as far as synthesis is concerned, but also challenges with respect to our ability to foresee molecular conformation and to establish sound structure−properties correlation in what at this point should be a well understood family of synthetic polymers. A cautious attitude should be maintained, nonetheless, because of possibly cooperative interplay of "minor" features in determining the polymorphic behavior and the crystalline morphology of specific polymers.

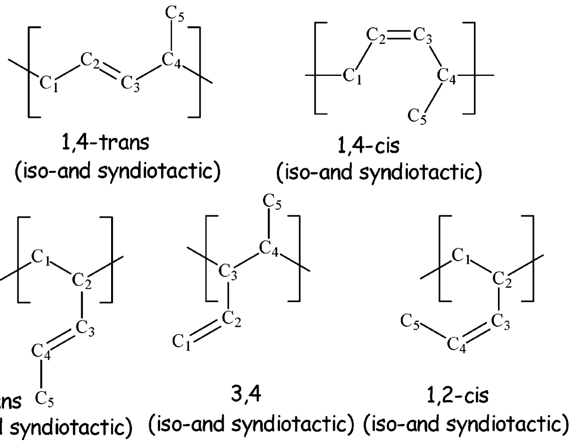

Figure 1. Possible stereoregular polymers obtainable from 1,3-pentadiene.

In the case of 1,3-pentadiene (*E* and *Z* monomers), 10 stereoregular polymers can, in principle, be obtained, which are displayed in Figure 1. A good part of them have already been described in the literature: *cis*-1,4 isotactic polypentadiene was synthesized from the (*E*) isomer with the system $AlEt_2Cl$−$Nd(OCOR)_3$−$Al(^iBu)_3$,[1] *cis*-1,4 syndiotactic polypentadiene was obtained from (*E*)-1,3-pentadiene with $Co(acac)_3$−$AlEt_2Cl$−H_2O[2] or $Co(acac)_3$−MAO,[3] *trans*-1,4 isotactic polypentadiene was obtained from the (*E*) isomer with the heterogeneous system VCl_3−$AlEt_3$,[4] and *cis*-1,2 syndiotactic polypentadiene was obtained by polymerizing (*Z*)-1,3-pentadiene with the system $CpTiCl_3$−MAO.[5] These four polymers were found to be crystalline by X-ray diffraction techniques, consistent with their substantial stereoregularity. Actually, a *trans*-1,2 polymer also was

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10.1021/ma047605q CCC: $30.25

prepared several years ago with the $Co(acac)_2-AlEt_2Cl$ system using heptane as solvent, but it was found to be amorphous.[6]

We have recently reported on the synthesis and the characterization of $CoCl_2(P^iPrPh_2)_2$ and its use, in association with methylaluminoxane (MAO), in the polymerization of butadiene to give a 1,2-syndiotactic polymer.[7] The same system was also used in the polymerization of substituted butadienes such as 1,3-pentadiene, 1,3-hexadiene, and 3-methyl-1,3-pentadiene, giving crystalline polymers that were found to exhibit a 1,2 structure on the basis of a preliminary IR and NMR characterization.[7]

We are specifically interested in the polymerization of different 1,3-dienes because, from the microstructure of the polymers obtained, useful information on the diene polymerization mechanism can be derived and the influence of monomer structure on the polymerization chemo- and stereoselectivity can be gauged. These features also carry an obvious significance with respect to possible copolymerization processes.

In this perspective, we are carrying out detailed studies of the above-mentioned polymers. In the present paper, we report specifically on the synthesis and the characterization by nuclear magnetic resonance (NMR, ^1H and ^{13}C), infrared spectroscopy (IR), X-ray diffraction, differential scanning calorimetry (DSC), and gel permeation chromatography (GPC) of the crystalline 1,2 polymer obtained from (*E*)-1,3-pentadiene. The crystalline structure of this new polymer has also been determined, and comparisons are drawn with those of other 1,2- and 3,4-polydienes previously reported (i.e., 1,2-syndiotactic polybutadiene,[8] 3,4-syndiotactic polyisoprene,[9] 1,2-syndiotactic poly(4-methyl-1,3-pentadiene),[10] and *cis*-1,2 syndiotactic polypentadiene[11]), highlighting the interplay between the structure and the conformation of the polymer main chain, the side-chain structure, and the crystalline architecture of the resulting macromolecule.

Experimental Section

Materials and Methods. $CoCl_2(P^iPrPh_2)_2$ was prepared as reported in the literature.[7] MAO (Crompton, 10 wt % solution in toluene) was used as received without further purification. Toluene (Carlo Erba, 99.5% pure) and heptane (Baker, >99.8% pure) were refluxed over Na for ca. 8 h, then distilled, and stored over molecular sieves under dry nitrogen. (*E*)-1,3-pentadiene (Aldrich, 99% pure) was refluxed for ca. 2 h over CaH_2, then distilled trap-to-trap and stored under dry nitrogen.

Polymerization. Heptane (14.2 mL), (*E*)-1,3-pentadiene (4 mL), and MAO (1×10^{-3} mol; 0.63 mL) were introduced in this order in a 50-mL dried flask. The solution thus obtained was brought to −30 °C, then $CoCl_2(P^iPrPh_2)_2$ (1×10^{-5} mol, 3 mL of a 2-mg/mL toluene solution) was added. All operations were carried out under dry nitrogen. The polymerization was terminated with methanol containing a small amount of hydrochloric acid after about one month. The polymer was coagulated and repeatedly washed with fresh methanol, then dried in a vacuum at room temperature (polymer yield, 68.6%).

Polymer Characterization. The IR spectra were recorded on a Bruker IFS 48 instrument using polymer films on KBr disks. The films were obtained by deposition from polymer solutions in hot benzene.

^{13}C and ^1H NMR measurements were carried out on Bruker AM 270 and Avance 400 spectrometers. The spectra were obtained in $C_2D_2Cl_4$ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt %.

Solid-state ^{13}C cross-polarization and magic-angle spinning (CPMAS) NMR experiments were recorded using a Bruker AVANCE spectrometer operating at 400 MHz for proton and a 4-mm double-bearing MAS probe. The experiments were recorded at room temperature with recycle times of 5 s, contact times of 1 ms, 90° pulse lengths of about 4 μs, spinning rate of 5 kHz and were transformed using a line broadening of 10 Hz. The number of scans (NS) are indicated in figure captions.

DSC scans were carried out on a Perkin-Elmer Pyris 1 instrument equipped with a liquid nitrogen subambient device. The sample, ca. 4 mg, was placed in a sealed aluminum pan, and the measurements were carried out using heating and cooling rates of 20 °C/min.

The molecular weight averages and the molecular weight distribution (MWD) were obtained by a high-temperature GPCV 2000 system (from Waters) using two on-line detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three Olefi columns from PSS, *o*-dichlorobenzene as the mobile phase, 0.8 mL/min of flow rate, and 145 °C of temperature. The calibration of the GPC system was constructed by eighteen narrow MWD polystyrene standards with the molar mass ranging from 162 to $3.3 \cdot 10^6$ g/mol.

X-ray diffraction patterns were recorded using graphite monochromated Cu Kα radiation ($\lambda = 1.54179$ Å) on a Bruker P4 diffractometer equipped with a HiStar 2D detector and with an air gun device for high-temperature measurements. The sample-to-detector distance was about 10 cm. A Bruker Nanostar system, equipped with mirror focusing, a HiStar 2D detector and a WAXS attachment with sample-to-detector distance of about 3 cm, and an Italstructres θ/θ diffractometer, using Ni-filtered Cu Kα radiation ($\lambda = 1.54178$ Å), with a high-temperature attachment to record the amorphous patterns, were also employed. The fiber repeat was also measured on a Weissenberg camera. Unoriented patterns were obtained using polymer powders or melt-crystallized chunks (ca. 1 mm^3). Oriented samples were prepared from films obtained, melting the polymer at ca. 180 °C, pressing it between glass slides, and quenching to room temperature in water. Strips 1-mm wide were then elongated to 200% at about 130−160 °C. Further annealing treatments did not show improvement of the degree of crystallinity of the samples.

Conformational Analysis. MM2 potential energy minima for the isolated main chain have been determined. The MM2 force field has been adopted in order to minimize spurious intrachain nonbonding interactions. The calculations have been carried out using 12 or 24 monomeric units chain fragments for the T_4 and the T_2G_2 main-chain conformation models. Starting backbone geometries with standard torsion angles, i.e., 60° and 180°, have been assumed. The number of monomeric units used in the calculations ensured minor terminal group effects, which were appropriately estimated and eliminated in the evaluation of final per monomer internal energies.

The MM2 results were confirmed by further molecular mechanics calculations involving periodical conditions applied to an infinite isolated main chain of appropriate symmetry. In this second step, the CVFF and PCFF force fields, as implemented into the Materials Studio package [Materials Studio and Discover are products of Accelrys Inc. (see www.accelrys.com)] were adopted.

Results and Discussion

(*E*)-1,3-pentadiene was polymerized at low temperature (−30 °C) and low MAO/Co molar ratio, using heptane as solvent, because these polymerization conditions were found to be optimal for the preparation of 1,2-syndiotactic polybutadiene with the system $CoCl_2(P^iPrPh_2)_2-MAO$.[7]

The synthesized polypentadiene has a substantial crystallinity (ca. 60−70%) as determined by comparison of the unoriented X-ray diffraction patterns recorded respectively at room temperature and above the melting

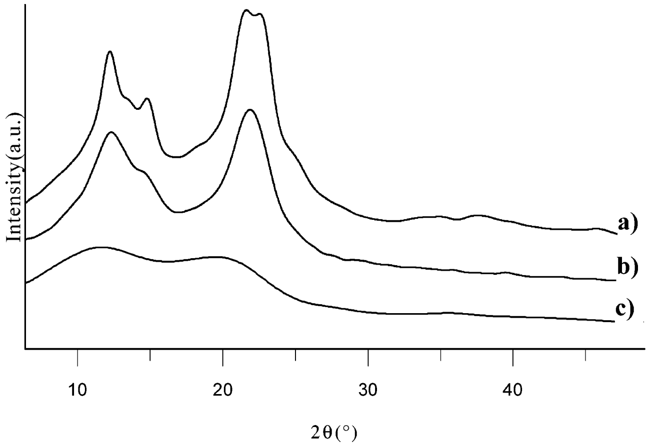


Figure 2. X-ray powder spectra of *trans*-1,2 syndiotactic polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO: (a) crystalline sample at room temperature, (b) sample quenched from the melt, and (c) molten sample.

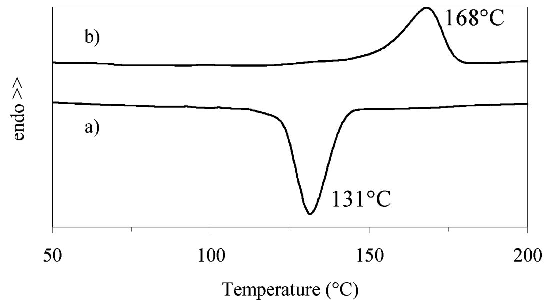


Figure 3. DSC thermograms of *trans*-1,2 syndiotactic polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO: (a) cooling scan and (b) heating scan both at rates of 20 °C/min.

point. (Figure 2, traces a and c). Samples quenched from the melt into ice−water exhibit diffraction patterns (Figure 2, trace b) that do not correspond either to the amorphous or to crystalline patterns, but rather suggest the possibility of intermediate stages of organization, characterized by highly disordered domains.

The high crystallinity and the ability to undergo relatively rapid crystallization is confirmed by the thermal behavior of the polymer; in Figure 3, successive DSC scans are displayed. The cooling run of the sample melted at 210 °C for 5 min (Figure 3a) shows an exothermic transition at 131 °C. In the successive heating scan (Figure 3b), an endothermic peak centered at 168 °C with a heat flow of 24.9 J/g is present. The polymer was also quenched from the melt into a liquid nitrogen bath and rapidly transferred in the DSC instrument kept at liquid nitrogen temperature. The heating run from −150 to +150 °C at 20 °C/min of the quenched sample did not show any thermal event preceding the melting endoherm (heat flow of about 25 J/g), and specifically, no clear evidence of a glass transition was also apparent with heating rates up to 40 °C/min. This could be due to insufficient sensitivity of the DSC technique, to the fact that the quenching procedure did not result in a sufficiently amorphous sample, or to inadequate transfer of the quenched sample to the DSC furnace.

The IR spectra of the polymer (Figure 4) could be straightforwardly interpreted according to well-established assignments reported in the literature.[12] No bands at 910 cm^{-1} (out-of-plane vibration of the hydrogen atoms adjacent to the double bond in a 3,4 unit), at 750 cm^{-1} (out-of-plane vibration of the hydrogen atoms adjacent to the double bond in a *cis*-1,4 unit), and at 727 cm^{-1} (out-of-plane vibration of the hydrogen atoms adjacent to the double bond in a *cis*-1,2 unit) were detected, demonstrating that these types of monomeric structures are not present in the polymer chain. On the contrary, two intense bands, respectively observed at 963 cm^{-1} (out-of-plane vibration of the hydrogen atoms adjacent to the double bond in a *trans*-1,2 unit) and 1376 cm^{-1} (vibration of the methyl groups in the *trans*-1,2 unit) (indicated in Figure 4), clearly suggest that the polymer has a *trans*-1,2 structure; the same bands are in fact at 966 and 1370 cm^{-1} in a polypentadiene having a *trans*-1,4 structure.

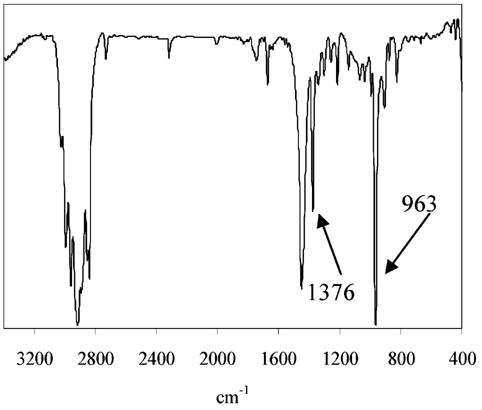


Figure 4. IR spectrum of *trans*-1,2 syndiotactic polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO.

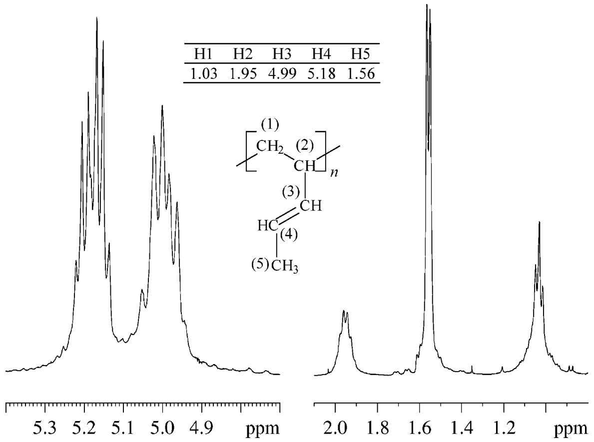


Figure 5. ^1H NMR spectrum of *trans*-1,2 syndiotactic poly(1,3-pentadiene) obtained with $CoCl_2(P^iPrPh_2)_2$−MAO.

The ^1H NMR spectrum of the polymer is shown in Figure 5. Peaks were assigned as indicated on the basis of chemical shift, integrals, and multiplicity. Specifically, the signal centered at 1.03 ppm, corresponding to the H1 methylene protons, is a false triplet, and it is indicative of a 1,2-syndiotactic structure. In fact, as reported in the literature for other syndiotactic polymers,[13] the two methylene protons are isochronous in a syndiotactic structure, being in equivalent environments. On the contrary, they are anisochronous in a 1,2-isotactic structure, giving rise to two different doublets of triplets.[14] The H4 olefin signal shows up as a doublet ($^3J_{CH=CH}$ = 15.2 Hz) of quartets ($^3J_{CH-CH3}$ = 6.3 Hz). The 15.2-Hz coupling constant confirms that the double bond has a trans configuration, in agreement with the IR results. Thus, both the IR and the ^1H NMR data indicate clearly that the polymer we obtained is *trans*-1,2 syndiotactic polypentadiene (t-12 sPPD).

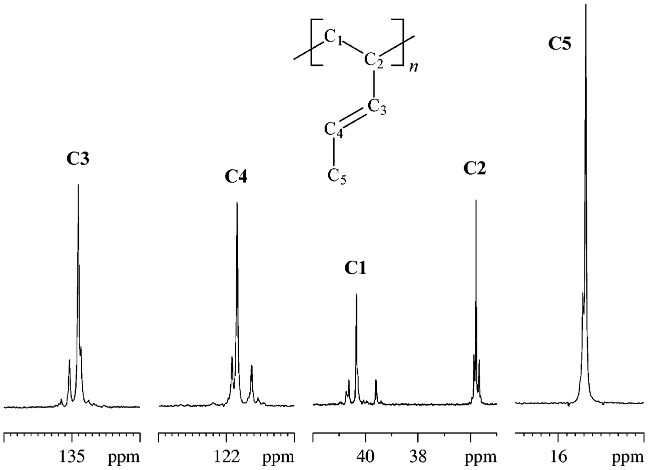


Figure 6. ^{13}C NMR spectrum of *trans*-1,2 syndiotactic polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO.

Figure 6 shows the ^{13}C NMR spectrum of t-12 sPPD. The five main resonances observed at 15.68, 35.79, 40.34, 121.84, and 134.90 ppm were assigned as indicated on the basis of the chemical shift values and the multiplicities of the proton undecoupled ^{13}C NMR spectrum (Figure 7). The ambiguity in the assignment of the two olefinic carbons was solved by calculating their chemical shifts using the Brouwer and Stothers approach,[15] starting from the experimental chemical shifts of the 1,2-syndiotactic polybutadiene olefin carbons (141.5 and 112.3 ppm for C3 and C4, respectively). By adding a methyl group, a $\beta\pi$ (−7.1 ppm) effect was considered on C3 and an $\alpha\pi$ (11.0 ppm) effect on C4. The calculated chemical shifts were 134.4 ppm for C3 and 123.3 ppm for C4, in good agreement with the experimental values of 134.9 and 121.8 ppm, respectively. The presence of some minor peaks around each of the main five peaks in the ^{13}C NMR spectrum (Figure 6) evidences the presence of different pentads arising from steric errors occurring upon the polymerization. Thus, by accepting the indication of the ^{1}H NMR spectrum concerning the syndiotactic character of the polymer, in the olefinic region, the main peak of C3 and C4 (134.91 and 121.84, respectively) will correspond to the *rrrr* pentad (about 60%), the other two (about 15% each) should correspond to the *rrrm* (134.87 and 121.91 for C3 and C4, respectively) and *rmrr* (135.04 and 121.63 for C3 and C4, respectively) pentads. In fact, the unique error *m* appears in the same amount in only these two pentads, one centered in the *rr* triad and the other centered in the *mr* triad. This observation suggests that the main error is represented by isolated *m* diads, which can be estimated at about 7−8%, suggesting that the average length of the syndiotactic sequence should be about 11 monomer units. Also, the C2 and C5 peaks reveal the presence of the above three pentads, while three different hexads can be observed for C1. Further work is in progress in order to completely assign the different signals corresponding to the different possible pentads.

The polymer was also analyzed by ^{13}C NMR in the solid state. The ^{13}C CPMAS spectrum is shown in Figure 8, where it is compared with that of *cis*-1,2 syndiotactic polypentadiene (c-12 sPPD).[11] The respective assignments are reported in Table 2. It is evident that both chemical shifts and carbon splitting differ for the two polymers. In the case of the *trans*-polymer, single resonances are observed, implying a unique environment for chemically equivalent carbons, in agreement with a *trans*-planar conformation. The observed splittings of the *cis*-polymer[11] are, on the contrary, found to arise from a conformation involving at least two different local environments of chemically equivalent carbons occurring in a more or less perturbed helical T_2G_2 main chain. Specifically, for the C1 methylene carbons, only one signal is observed in the trans polymer, as expected for *tttt* sequences, in which the methylene carbon is always trans to the C2 methine carbons, while two signals with an 8-ppm splitting are observed in the cis polymer because of the presence of two conformationally distinct methylenes with two and zero γ-gauche interactions, respectively.

The above analysis regarding the tacticity and the main-chain conformation of t-12 sPPD is unequivocally supported by X-ray fiber-diffraction patterns (Figure 9), which exhibit a periodicity of 5.14 ± 0.03 Å, consistent with a *trans*-planar main-chain conformation, which, assuming a 1,2 connectivity, implies a syndiotactic stereochemistry. The diffraction maxima in the fiber pattern and in the unoriented patterns closely correspond, indicating that the polymer is found in the same crystal modification both in oriented and in unoriented samples (see Table 3 for a list of the observed diffraction maxima). The fiber diffraction patterns

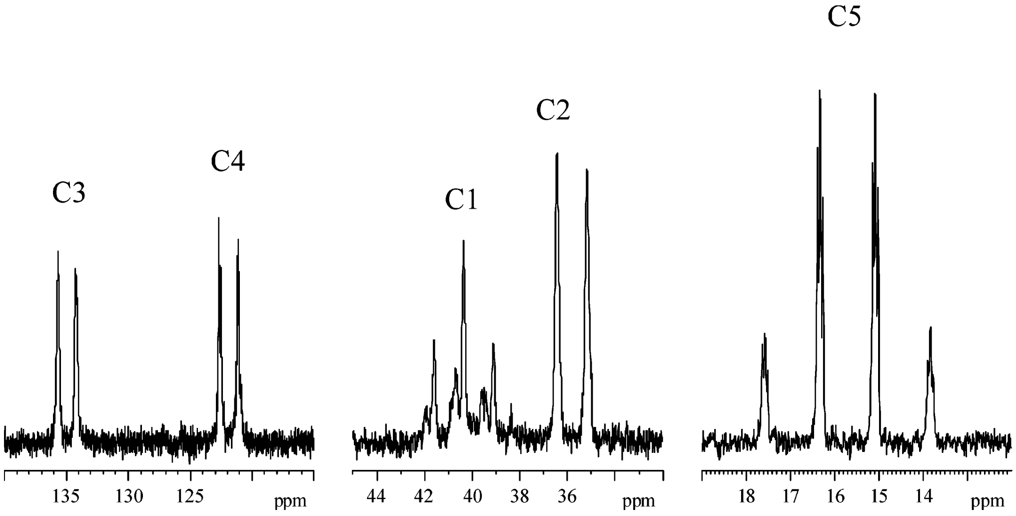


Figure 7. Proton undecoupled ^{13}C NMR spectrum of *trans*-1,2 syndiotactic polypentadiene obtained with $CoCl_2(P^iPrPh_2)_2$−MAO.

Table 1. Polymerization of (*E*)-1,3-Pentadiene with CoCl$_2$(P^{i}PrPh$_2$)$_2$–MAO

polymerization[a]		polymer microstructure[b]					
time (d)	yield %	1,2-*trans* %	[*rrrr*] %	M_{w}[c] g/mol	*D*[c]	mp[d] °C	identity period Å
30	68.6	~99	60	167000	2.5	168	5.14

[a] Polymerization conditions: heptane, 14.2 mL; (*E*)-1,3-pentadiene, 4 mL; MAO, 1 × 10^{-3} mol; CoCl$_2$(P^{i}PrPh$_2$)$_2$, 1 × 10^{-5} mol; −30 °C. [b] Determined by ^{13}C and ^{1}H NMR analysis. [c] Molecular weight and molecular weight distribution, determined by GPC analysis. [d] Melting point, determined by DSC analysis.

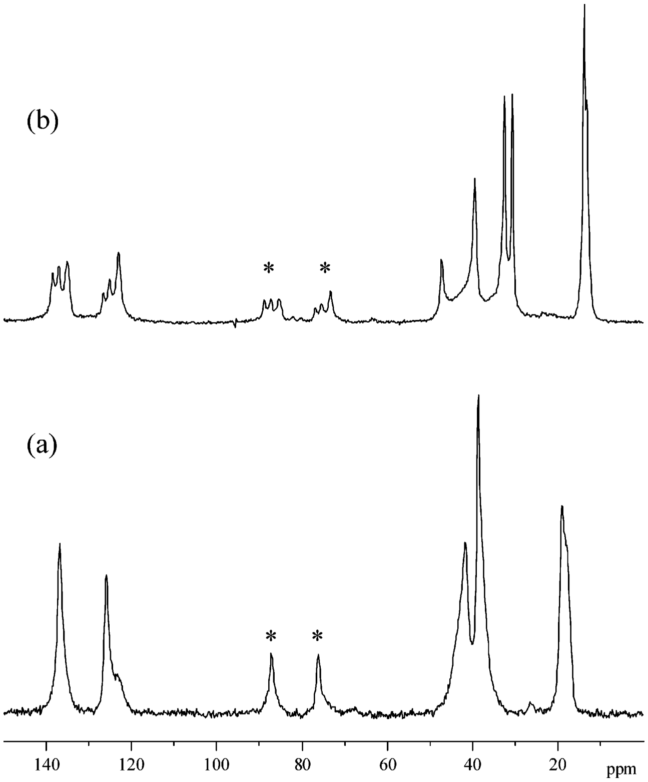
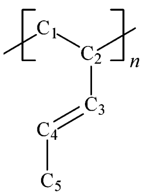
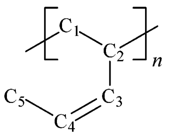


Figure 8. ^{13}C CPMAS NMR spectra of (a) *trans*-1,2 syndiotactic polypentadiene, NS 224, and (b) *cis*-1,2 syndiotactic polypentadiene, NS 2000. Spinning sidebands are indicated by (∗).

Table 2. Assignment of the Solid-State ^{13}C CPMAS Spectra of *trans*- and *cis*-1,2[11] Syndiotactic Polypentadienes

Carbon	δ in ppm	
		
C1	41.82	47.37 39.48
C2	38.75	32.61 30.71
C3	136.68	138.58 136.97 135.07
C4	125.87	126.60 125.13 123.09
C5	19.17	13.90 13.32

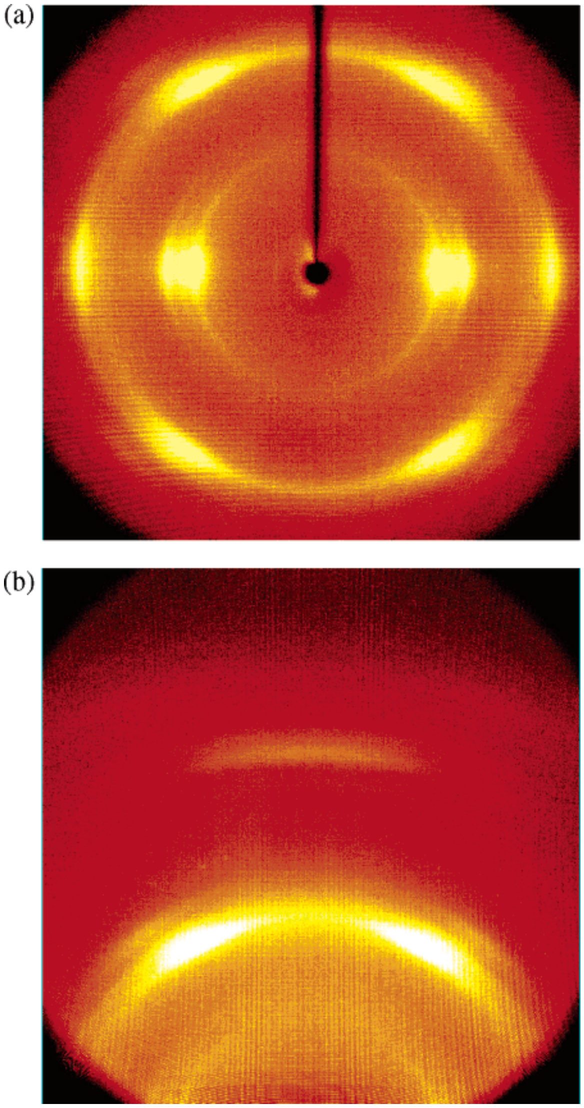


Figure 9. Normal-beam fiber diffraction patterns (fiber vertical) of *trans*-1,2 syndiotactic polypentadiene: (a) lower angle, (b) higher angle pattern of meridional area.

further indicate rather small disordered crystals. This is in qualitative agreement with the ^{13}C NMR data, suggesting that stereoregular sequences are frequently interrupted by errors and, hence, that crystallizable sequences are relatively short.

Molecular mechanics calculations with the MM2, the CVFF, and the PCFF force fields consistently confirm that the all-trans conformation (Figure 10a) is more stable than the T$_2$G$_2$ conformation by about 0.5 kcal/(mol CRU), a difference that can be considered significant with confidence. Calculations adopting MM2 were carried out without symmetry constraints. In a second step, the CVFF and PCFF force fields as implemented in the Materials Studio package were used, and by imposing glide symmetry with a 5.14 Å periodicity was imposed to the all-*trans* conformation. Similarly, a rigorous 2_1 symmetry with a 7.5 Å periodicity was used to examine the (T$_2$G$_2$)$_2$ conformation. Because it is very likely that the more extended conformations, i.e., the

Table 3. List of the Observed Maxima in Powder and in Fiber Diffraction Patterns[a]

powders		fiber		calculated	
d (Å)	intensity	*d* (Å)	intensity	*hkl*	*d* (Å)
7.25	vs	7.25	vs	020	7.32
6.60	s	6.56	s	100	6.59
6.01	s	5.95	s	110	6.01
4.90	w	5.01	w	120	4.90
4.09	ws	4.12	vs	021	4.23
				101	4.07
3.94	vs	3.94	s	111	3.92
				130	3.92
3.55	w	3.54	mw	121	3.56
				031	3.55
3.15	w			140	3.20
				131	3.12
		2.70	vvw	141	2.72
2.66	w	2.66	w	150	2.67
2.55	w			002	2.59
				012	2.55
		2.44	w/vw	231	2.42
2.38	w	2.37	w	112	2.38
		2.27	w	032	2.29
		2.20	vvw	250	2.19
		1.99	vw	222	1.96
1.98	w	1.98	w	170	1.99
				260	1.96

[a] *D*-spacings and tentative indexing and of the diffraction maxima calculated assuming an orthorhombic lattice with a = 6.60, b = 14.65, and c = 5.18 Å are also listed.

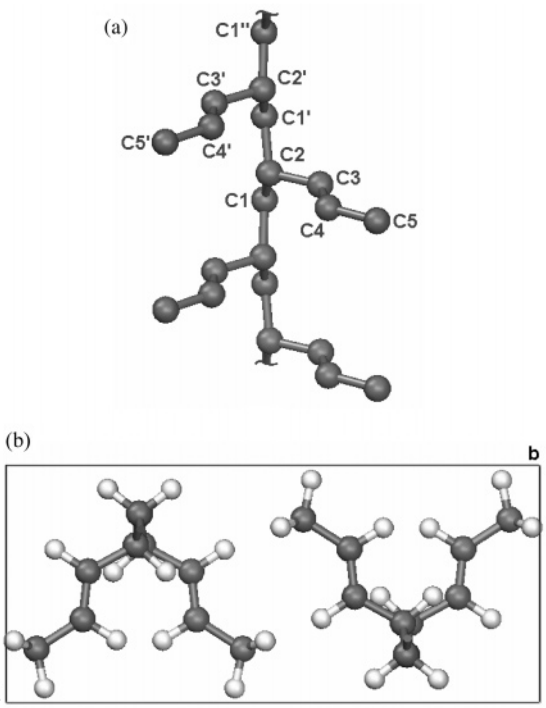


Figure 10. Crystal conformation of *trans*-1,2 syndiotactic polypentadiene (a) and packing (b) viewed down the c axis.

all-trans main-chain conformations, will also have larger intermolecular packing contributions; the calculations are fully consistent with the experimental diffraction and spectroscopic results, which evidence that *trans*-1,2 syndiotactic polypentadiene adopts a *trans*-planar crystalline conformation. Figure 10 convincingly shows that the steric conflicts between the methyls of adjacent side chains, which inhibit the cis isomer to adopt this conformation,[11] do not occur in the case of the trans polymer. Note that a key simplifying feature is that the conformational minimum of the side chain, due to the sp^2 hybridization of C3 and C4 in 1,2-polydienes, is for both polymers very close to skew, i.e., with C4 nearly eclipsed to the hydrogen on C2. In the case of *trans*-1,2 syndiotactic polypentadiene, more complex main-chain structures, such as the $T_6G_2T_2G_2$, were not investigated at this stage, but given the above considerations, they appear unlikely in stable crystalline modifications.

Crystal Structure Determination and Refinement

The relatively few and rather broad fiber diffraction data (Figures 2 and 9) allow a tentative indexing of diffraction patterns with an orthorhombic lattice with a = 6.6 Å, b = 14.7 Å, and c = 5.14 Å. A list of the observed and calculated diffraction maxima present in the fiber and in the powder patterns with the indexing are reported in Table 3. With four monomer units in the unit cell, a calculated density of 0.91 g/cm^3 is obtained, fully consistent with the experimental value of 0.90 g/cm^3 determined by flotation. Taking into account the similarities of the system under study with 1,2-syndiotactic polybutadiene (1,2sPBD),[8] packing models in space group *Pbcm* were examined. This space group was found plausible in the case of 1,2sPBD and more recently for 3,4-syndiotactic polyisoprene.[9] Powder pattern calculations performed with this high symmetry showed rough but encouraging agreements between the main features of the observed and calculated profiles.

Efforts concentrated on ordered and disordered *Pbcm* models, but models in the lower symmetry subgroup $P2_1/c$, which satisfy most systematic absences suggested by the diffraction data while allowing for greater conformational freedom, were also examined. In all the examined cases, consistent with solid-state NMR evidence, the chemical repeat unit coincides with the asymmetric unit.

The crystal structure of t-12 sPPD was refined using the Rietveld technique, i.e., by the best fitting of the whole X-ray powder pattern profile. The program "Debvin",[16–18] which allows for constrained refinements using available a priori structural information such as bond lengths and angles, was used throughout. In the *Pbcm* space group, the lattice parameters refined to the following values: a = 6.60(1) Å, b = 14.63 (1) Å, and c = 5.11(3) Å, yielding a calculated density of 0.91 g/cm^3.

$P2_1/c$ models and disordered *Pbcm* models were also refined. In $P2_1/c$, only the glide plane relating successive monomers in a chain is preserved. No other intramolecular symmetry operators exist: neither the mirror plane perpendicular to the main chain, on which the side-chain and the tertiary main-chain carbon atom must lie, nor the binary axis through the main-chain methylene, which occur in the ordered *Pbcm* model. Thus, the number of independent structural refinable parameters nearly doubles. In disordered *Pbcm* models chains present the same intramolecular symmetry, and as a consequence, the number of refinable parameters is closely similar as in $P2_1/c$. Two chains related by a mirror plane at z = 0.25 and with a 0.5 occupancy are statistically copresent at each site. However, no significant agreement improvement was obtained with either the $P2_1/c$ or the disordered *Pbcm* models over the refinement using the highly constrained, ordered *Pbcm* models. As a consequence only the results with the latter choice will be discussed.

In Table 4, all the refined internal coordinates for *trans*-1,2 syndiotactic polypentadiene are listed, while

Table 4. Refined Internal Coordinates for *trans*-1,2 Syndiotactic Polypentadiene[a]

	bond lengths (Å)		
C1−C2	1.544[b]	C2−C3	1.529[b]
C3−C4	1.338[b]	C4−C5	1.515[b]
	bond angles (deg)		
C1−C2−C1′	111.6	C2−C1′−C2′	111.8
C1−C2−C3	107.3	C2−C3−C4	123.4
C3−C4−C5	127.6		
	torsion angles (deg)		
C1−C2−C1′−C2′	−175.4	C2′−C1′−C2−C3	67.4
C1−C2−C3−C4	120[b]	C2−C3−C4−C5	−180[b]

[a] Estimated standard deviations vary between 0.3 and 1.0° for bond angles, and between 1.0 and 2.0° for torsion angles. [b] Values not refined.

Table 5. Refined Atomic Parameters of Non-hydrogen Atoms in *trans*-1,2 Syndiotactic Polypentadiene

	X	Y	Z	B (Å^2)
C1	0.2078	0.2501	0.0000	4.0
C2	0.3390	0.2461	0.2500	4.0
C3	0.4480	0.1539	0.2500	4.0
C4	0.6500	0.1454	0.2500	4.0
C5	0.7725	0.0578	0.2500	4.0

in Table 5, we report the final fractional atomic coordinates of all non-hydrogen atoms. Views of the refined molecular conformation and of the packing are shown in Figure 10. The final disagreement factor R_2' ($R_2' = \Sigma|I_{\text{obs}} - I_{\text{calc}}|/\Sigma I_{\text{net}}$ where $I_{\text{net}} = I_{\text{obs}} - I_{\text{bkg}}$) is 0.058 with the ordered *Pbcm* space group. In Figure 11, the observed (a) and calculated (b) profiles are reported together with the difference curve (c).

Standard bond lengths reported in Table 4 were adopted without further refinement. The C1−C2−C1′and C2−C1′−C2′ bond angles on the main chain were initially set to 111° and 114°, respectively, and constrained refinement was allowed. The refined values of these and the other refined bond angles are in reasonable agreement with those of common hydrocarbon polymers, with the exception of the C2−C3−C4 and the C3−C4−C5 bond angles, whose large values (123.4° and 127.6° respectively) suggest some side-chain disorder. Hydrogen atoms were located at calculated positions after completing a few refinement cycles.

A number of nonstructural parameters were refined as well and are listed in Table 6. A zero correction was applied to the whole profile pattern. The background level was obtained as a segmented line with 12 nodes separated by 3−4° on the 2θ scale and refined on the intensity scale but constrained to follow qualitatively the amorphous diffraction pattern (see Figure 2). A Cauchy function was used to fit peak shapes; peak asymmetry was assumed and described using two half-peak functions with different half-height widths. A preferred orientation parameter was taken into account along the 001 direction, yielding, as expected, a minor degree of orientation.

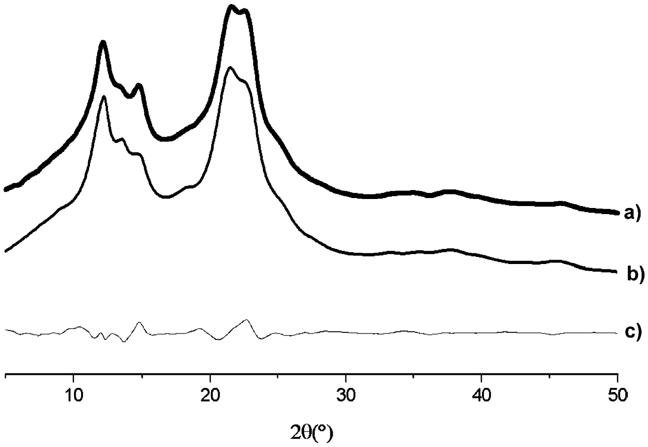


Figure 11. Unoriented X-ray diffraction pattern of *trans*-1,2 syndiotactic polypentadiene: (a) observed profile, (b) calculated profile, and (c) difference curve.

Table 6. Refined Nonstructural Parameters

zero correction (2θ) (deg)	−0.1044
profile function parameters[a]	
U	−20.00956
V	21.73605
W	0.91165
A[b]	49.7006
preferred orientation parameter[c]	
G	0.17529
background parameters	
segmented line points location 2θ°	intensity (counts 10^{-3})
6	0.4830
9	0.9039
12	0.8522
15	1.1206
19	1.0185
23	0.9043
27	0.3566
31	0.2752
35	0.1082
39	0.0895
43	0.0658
47	0.0236
average crystallite dimensions (Å)	
L_{a}	50.0
L_{b}	120.0
L_{c}	35.0

[a] Peak shapes are calculated analytically through a Cauchy function: $f(z) = (C/H_k)[1 + 4z^2]^{-1}$; with $z = (2i - 2_k)/Hk$ and $H_k^2 = U \tan^2\theta_k + V \tan\theta_k + W$. [b] Peak asymmetry is accounted for by splitting a peak into two halves with different FWHM, so that $H_k' - H_k'' = 2(A/(2\theta)^2)$, where A is a refinable parameter. [c] Preferred orientation parameter is $PO = \exp(-G\alpha_k^2)$ where α_k is the angle between the scattering vector of the kth reflection and the scattering vector of a fixed (the preferred) reflection of indices $h'k'l'$ given in the input file, in this case 001.

Crystallite dimensions were also refined: half-height widths of each reflection in the whole diffraction profile are considered directly related to the Miller indices *hkl* and to the mean crystallite dimensions along the three crystallographic axes.[19,20] Refinement of U, V, and W parameters in the Caglioti-Cox[21] equation led to values of coherence lengths (crystallite dimensions) of about 50, 120, and 35 Å along a, b, and c respectively. It is interesting that the thickness along c compares well with the mean length of the syndiotactic sequence, in fact it is ca. 20% larger, suggesting that the crystals may include some, but relatively few, defective units.

The shortest intramolecular distances between non-hydrogen atoms separated by more than three bonds are 3.65 Å (C2···C4′), while the C4···C4′ distance measures 4.01 Å (see Figure 10a). Intermolecular distances allow easily the coexistence of the two chains in the unit cell: the shortest contacts between non-hydrogen atoms measure 4.19 and 4.23 Å, respectively, and involve the C1 methylene carbon with the C4 atoms and the C5 atoms of the asymmetric unit separated by one a lattice vector translation. Slightly longer packing distances of 4.29 Å are found between the C3 and the C5 atoms of chains separated by 0.5 *b*. The shortest intermolecular H···H contacts are 2.39 and 2.37 Å, respectively, for molecules separated respectively by one *a* lattice vector translation and by 0.5 *b*. The relatively loose packing suggests the possibility of some side-chain disorder, as already suggested by commenting on bond angle values.

Conclusions

A crystalline *trans*-1,2 syndiotactic polypentadiene was obtained for the first time by polymerizing (*E*)-1,3-pentadiene with the system $CoCl_2(P^iPrPh_2)_2$−MAO; a *trans*-1,2 polypentadiene had already been obtained several years ago with the system $Co(acac)_3$−$AlEt_2Cl$−H_2O, but it was found to be amorphous.[6]

The NMR, X-ray, and IR characterization of the polymer consistently show that *trans*-1,2 syndiotactic polypentadiene strongly favors an all-trans main-chain conformation. This behavior is closely related to those evidenced for 1,2-syndiotactic polybutadiene[8] and 3,4-polyisoprene,[9] both of which carry sp^2 CH_2-terminated side chains. The preference of *trans*-1,2 syndiotactic-polypentadiene for the all-trans main-chain conformation is also apparent from molecular mechanics isolated chain calculations, showing this extended conformation to be the most favorable. The situation significantly differs from the one found for the closely related *cis*-1,2 syndiotactic polypentadiene[11] and in the case of 1,2-syndiotactic poly(4-methyl-1,3-pentadiene),[10] for which $T_6G_2T_2G_2$ and T_2G_2 chain conformations show comparable energies significantly more stable than the T_4 main-chain conformation. In particular, the crystalline main-chain conformations of *cis*-1,2 syndiotactic polypentadiene and syndiotactic 1,2-poly(4-methyl-1,3-pentadiene) are found to be a perturbed T_2G_2 and $T_6G_2T_2G_2$, respectively. All these results can be qualitatively rationalized in terms of the repulsive interactions occurring with a *trans*-planar main-chain conformation between the terminal methyls of adjacent chemical repeats with a cis but not with a trans double-bond configuration in the side chains.

Acknowledgment. Mr. Giulio Zannoni, Mrs. Fulvia Greco, and Mr. Alberto Giacometti Schieroni are acknowledged for skillful assistance in NMR and GPC analyses of the polymers.

References and Notes

(1) (a) Natta, G.; Porri, L.; Stoppa, G.; Allegra, G.; Ciampelli, F. *J. Polym. Sci., Part B* **1963**, *1*, 67. (b) Natta, G.; Porri, L.; Carbonaro, A.; Stoppa, G. *Makromol. Chem.* **1964**, *77*, 114. (c) Cabassi, F.; Italia, S.; Ricci, G.; Porri, L. In *Transition Metal Catalyzed Polymerization*; Quirk, R. P., Ed.; Harwood Academics: New York, **1988**; pp 655−670. (d) Purevsuren, B.; Allegra, G.; Meille, S. V.; Farina, A.; Porri, L.; Ricci, G. *Polym. J.* **1998**, *30*, 431.

(2) (a) Porri, L.; Carbonaro, A. *Makromol. Chem.* **1963**, *60*, 236. (b) Natta, G.; Porri, L.; Carbonaro, A.; Ciampelli, F.; Allegra, G. *Makromol. Chem.* **1962**, *51*, 229.

(3) Ricci, G.; Italia, S.; Comitani, C.; Porri, L. *Polym. Commun.* **1987**, *28*, 223.

(4) (a) Natta, L.; Porri, L.; Corradini, P.; Morero, D. *Chim. Ind. (Milan)* **1958**, *40*, 362. (b) Natta, G.; Porri, L.; Corradini, P.; Zanini, G.; Ciampelli, F. *J. Polym. Sci.* **1961**, *51*, 463.

(5) Ricci, G.; Italia, S.; Porri, L. *Macromolecules* **1994**, *27*, 868.

(6) (a) Natta, G.; Porri, L.; Sovarzi, G. *Eur. Polym. J.* **1965**, *1*, 81. (b) Porri, L.; Di Corato, A.; Natta, G. *Eur. Polym. J.* **1969**, *5*, 1.

(7) Ricci, G.; Forni, A.; Boglia, A.; Motta, T.; Zannoni, G.; Canetti, M.; Bertini, F. *Macromolecules* **2005**, *38*, 1064.

(8) Natta, G.; Corradini, P. *J. Polym. Sci.* **1956**, *20*, 251.

(9) (a) Bazzini, C.; Giarrusso, A.; Porri, L.; Pirozzi, B.; Napolitano, R. *Polymer* **2004**, *45*, 2871. (b) Pirozzi, B.; Napolitano, R.; Petraccone, V.; Esposito, S. *Macromol. Chem. Phys.* **2004**, *205*, 1343.

(10) (a) Meille, S. V.; Capelli, S.; Ricci, G. *Macromol. Rapid Commun.* **1995**, *16*, 891. (b) Immirzi, A.; Tedesco, C.; Meille, S. V.; Famulari, A.; van Smaalen, S. *Macromolecules*, **2003**, *36*, 3666.

(11) Ricci, G.; Alberti, E.; Zetta, L.; Motta, T.; Bertini, F.; Mendichi, R.; Arosio, P.; Famulari, A.; Meille, S. V. *Macromolecules* **2005**, *38*, 8353.

(12) (a) Natta, G.; Porri, L.; Corradini, P.; Zanini, G.; Ciampelli, F. *J. Polym. Sci.* **1961**, *51*, 463. (b) Natta, G.; Porri, L.; Carbonaro, A.; Stoppa, G. *Makromol. Chem.* **1964**, *77*, 114. (c) Ciampelli, F.; Lachi, M. P.; Tacchi Venturi, M.; Porri, L. *Eur. Polym. J.* **1967**, *3*, 353. (d) Porri, L.; Di Corato, A.; Natta, G. *Eur. Polym. J.* **1969**, *5*, 1. (e) Beebe, D. H.; Gordon, C. E.; Thudium, R. N.; Throckmorton, M. C.; Hanlon, T. L. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2285.

(13) (a) Zambelli, A.; Giongo, M. G.; Natta, G. *Makromol. Chem.* **1968**, *112*, 183. (b) See, for instance: Bovey, F. A. *High-Resolution NMR of Macromolecules;* Academic Press: New York, 1972.

(14) Ricci, G.; Porri, L. *Polymer* **1997**, *38*, 4499.

(15) Brouwer, H.; Stothers, J. B. *Can. J. Chem.* **1972**, *50*, 1361.

(16) Immirzi, A. *Acta Crystallogr.* **1980**, *B36*, 2378.

(17) Millini, R.; Perego, G.; Bruckner, S. *Mater. Sci. Forum* **1991**, *71*/*82*, 239.

(18) Bruckner, S.; Immirzi, A. *J. Appl. Crystallogr.* **1997**, *30*, 207.

(19) Allegra, G.; Bassi, I. W.; Meille, S. V. *Acta Crystallogr.* **1978**, *A34*, 652.

(20) Perego, G.; Cesari, M.; Allegra, G. *J. Appl. Crystallogr.* **1984**, *17*, 403.

(21) Caglioti, G.; Paoletti, A.; Ricci, F. P. *Nucl. Instrum. Methods* **1958**, *3*, 223.

MA047605Q