Isotactic and Syndiotactic Alternating Ethylene/Propylene Copolymers Obtained Through Non-Catalytic Hydrogenation of Highly Stereoregular cis-1,4 Poly(1,3-diene)s

Giovanni Ricci 1,* , Antonella Caterina Boccia 1, Giuseppe Leone 1, Ivana Pierro 1,2, Giorgia Zanchin 1,3, Miriam Scoti 2, Finizia Auriemma 2 and Claudio De Rosa 2

1 CNR-Istituto per lo Studio delle Macromolecole (ISMAC), Via A. Corti 12, I-20133 Milano, Italy; antonella.boccia@ismac.cnr.it (A.C.B.); giuseppe.leone@ismac.cnr.it (G.L.); ivana.pierro@ismac.cnr.it (I.P.); giorgia.zanchin@ismac.cnr.it (G.Z.)
2 Dipartimento di Scienze Chimiche, Università di Napoli Federico II, Complesso Monte S. Angelo, Via Cintia, I-80126 Napoli, Italy; miriam.scoti@unina.it (M.S.); auriemma@unina.it (F.A.); claudio.derosa@unina.it (C.D.R.)
3 Dipartimento di Chimica, Università degli Studi di Milano, via C. Golgi 19, I-20133 Milano, Italy
* Correspondence: giovanni.ricci@ismac.cnr.it; Tel.: +39-02-23699376

Abstract: The homogeneous non-catalytic hydrogenation of cis-1,4 poly(isoprene), isotactic cis-1,4 poly(1,3-pentadiene) and syndiotactic cis-1,4 poly(1,3-pentadiene) with diimide, formed by thermal decomposition of para-toluenesulfonylhydrazide, is examined. Perfectly alternating ethylene/propylene copolymers having different tacticity (i.e., isotactic and syndiotactic), which are difficult to synthesize by stereospecific copolymerization of the corresponding monomers, are obtained. Both isotactic and syndiotactic alternating ethylene/propylene copolymers are amorphous, with very low glass transition temperatures.

Keywords: ethylene/propylene copolymers; hydrogenation; NMR; XRD

1. Introduction

Nowadays ethylene/propylene (E/P) copolymers are one of the most important families of polymeric materials, with endless applications. The performance of E/P copolymers can be easily tuned by varying the comonomer composition, comonomer distribution and chain stereoregularity. When the comonomers are randomly distributed, amorphous polymers (E/P rubbers and E/P/diene rubbers), emerging as a new class of thermoplastic elastomers, can be obtained [1]. If the comonomer is isolated, crystalline copolymers result, which are widely used as impact-strength modifiers in blends with isotactic poly(propylene) [2].

The synthesis of alternating E/P copolymers has been one of the challenging subjects of both practical and fundamental interest in recent years [3]. The development of metallocene [4], and post-metallocene complexes [5] for olefin polymerization has opened new opportunities for the synthesis of alternating copolymers with controlled microstructure and properties. Alternating E/P copolymers have been obtained by the copolymerization of ethylene with propylene with some ansa-zirconocenes-based catalysts [6–8], and by living polymerization of 1-pentene with an α-dimine Ni(II) catalyst through a controlled chain-walking mechanism [9].

An alternative route for the synthesis of perfectly alternating ethylene/α-olefin copolymers in general, and of E/P copolymers in particular, is the one taking advantage of the hydrogenation
of stereoregular poly(1,3-diene)s with 1,4-structure (cis-1,4 and trans-1,4 poly(1,3-pentadiene)s and poly(isoprene)s in case of E/P copolymers). In recent years we have introduced novel catalyst systems, based on different types of transition metal and lanthanide complexes with various ligands (e.g., phosphines, imines, pyridinimines, ketoimines) and methylaluminoxanes [9–13], which allowed some of us to synthesize and completely characterize highly stereoregular poly(1,3-diene)s with different structures (e.g., iso- and syndiotactic cis poly(isoprene)s in case of E/P copolymers). In recent years we have introduced novel catalyst systems, based on different types of transition metal and lanthanide complexes with various ligands (e.g., phosphines, imines, pyridinimines, ketoimines) and methylaluminoxanes [9–13], which allowed some of us to synthesize and completely characterize highly stereoregular poly(1,3-diene)s since, at least in principle, it could allow one to get through the hydrogenation process: (i) highly stereoregular iso- and syndiotactic poly(α-olefin)s from highly stereoregular 1,2 and 3,4 poly(1,3-diene)s (Scheme 1); and (ii) perfectly alternating ethylene/α-olefin copolymers from highly stereoregular cis-1,4 and trans-1,4, iso- and syndiotactic, poly(1,3-diene)s (Scheme 2), which in some cases are unlikely to the obtainable through the simple stereo-specific homo- and co-polymerization of the corresponding monomers. We have recently reported the synthesis and characterization of: (i) isotactic poly((R,S)-3-methyl-1-pentene) obtained by hydrogenation of isotactic 1,2 poly((E)-3-methyl-1,3-pentadiene) [29,30], and (ii) ethylene/2-butene copolymers obtained by hydrogenation of some cis-1,4 and trans-1,4 highly stereoregular poly(1,3-diene)s [31].

**Scheme 1.** Saturated α-olefin polymers which, at least in principle, can be obtained by hydrogenation of poly(1,3-diene)s with a 1,2 structure (4M1P = 4-methyl-1-pentene, 3M1P = 3-methyl-1-pentene, 5M1H = 5-methyl-1-hexene, 3M1B = 3-methyl-1-butene).

**Scheme 2.** Saturated α-olefin (co)polymers which, at least in principle, can be obtained by hydrogenation of cis-1,4 poly(1,3-diene)s. In bold the alternating E/P copolymer object of the present investigation. Poly(E-alt-2-butene) can be also obtained with \( R_1 = R_2 = \text{Me} \) and \( R_3 = \text{H} \).
In the present paper, we report the preparation and characterization of perfectly alternating ethylene/propylene iso- and syndiotactic copolymers, obtained by hydrogenation of the following three highly stereoregular poly(1,3-diene)s: isotactic cis-1,4 poly(1,3-pentadiene), syndiotactic cis-1,4 poly(1,3-pentadiene), and cis-1,4 poly(isoprene).

2. Results and Discussion

The highly stereoregular poly(1,3-diene)s on which this study focused were: syndiotactic cis-1,4 poly(1,3-pentadiene) [hereafter named sP(EP)], isotactic cis-1,4 poly(1,3-pentadiene) [iP(EP)] and cis-1,4 poly(isoprene) (PI). iP(EP) and PI were obtained by polymerizing (E)-1,3-pentadiene and isoprene, respectively, with the ternary catalyst system AlEt$_2$Cl/Nd(OCOC$_7$H$_{15}$)$_3$/Al$i$Bu$_3$, as described in [21,32,33], respectively. The sP(EP) was synthesized with catalyst CoCl$_2$(P$_t$Bu$_2$Me)$_2$/MAO as described in [34]. The polymerization data are summarized in Table 1.

| Sample | Monomer | Catalyst | Time (min) | Yield (%) | cis-1,4 (%) | $T_g$ ($^\circ$C) |
|--------|---------|----------|------------|-----------|------------|-----------------|
| iP(EP) | (E)-1,3-pentadiene | AlEt$_2$Cl/Nd(OCOC$_7$H$_{15}$)$_3$/Al$i$Bu$_3$ | 60 | 87 | ≥90 | −66 |
| sP(EP) | (E)-1,3-pentadiene | CoCl$_2$(P$i$Bu$_2$Me)$_2$/MAO | 144 | 69 | ≥99 | −66 |
| PI | isoprene | AlEt$_2$Cl/Nd(OCOC$_7$H$_{15}$)$_3$/Al$i$Bu$_3$ | 30 | 100 | ≥97 | −65 |

1 polymerization conditions: monomer (2 mL); heptane (total volume 16 mL) (or toluene in the case of sP(EP)), Co or Nd complex, $2 \times 10^{-5}$ mol; temperature, 22 °C; 2 Percentage of cis-1,4 units, determined by NMR analysis; 3 determined by DSC.

The hydrogenation of the above polymers was then examined. There are different methods to hydrogenate poly(1,3-diene)s which involve both catalytic and non-catalytic ways [35]. Catalytic hydrogenation is the conventional one, but it has some drawbacks such as: (i) the high cost of the equipment, (ii) the use of expensive hydrogenation conditions, which are mostly associated with high pressure reactors and expensive catalyst, and (iii) the low efficiencies resulting from limited solubility of the reagents. Alternatively, the hydrogenation of unsaturated polymers by a non-catalytic way, in which the reaction is promoted by diimide (diazenes, NH=NH), has been shown to be an attractive process and extremely efficient in the case of 1,3-diene polymers [36,37].

In this work, we exploited the non-catalytic hydrogenation of the target stereoregular poly(1,3-diene)s with diimide in homogeneous conditions at 120 °C in o-xylene (Scheme 3). Diimide was generated in situ through the thermolysis of p-toluenesulfonic acid (TSH) [38]. The hydrogenation process converted iso- and syndiotactic cis-1,4 poly(1,3-pentadiene)s and cis-1,4 poly(isoprene) into perfectly alternating E/P copolymers (Scheme 3), having iso- or syndiotactic structures depending on the starting unsaturated polymer. Hereafter, we will name the alternating E/P copolymers from the hydrogenation of the corresponding 1,3-diene polymers as H-sP(EP), H-iP(EP) and H-PI, respectively.

The complete hydrogenation of the diene polymers was confirmed by comparison of FTIR and $^1$H-NMR spectra of the starting cis-1,4 poly(1,3-diene)s and of the corresponding hydrogenated products (Figures 1 and 2, respectively).

The typical bands observed at 746 cm$^{-1}$ in the FTIR spectra of cis-1,4 poly(1,3-pentadiene)s and 840 cm$^{-1}$ in the FTIR spectra of cis-1,4 poly(isoprene), ascribed to the out-of-plane vibration of the hydrogen atoms adjacent to the double bond in a cis-1,4 unit, are completely absent in the FTIR spectra of the corresponding saturated polymers; besides, a new band at 735 cm$^{-1}$ was observed in the FTIR spectra of the hydrogenated polymers, ascribed to the vibration of a −CH$_2$− unit, typical of saturated polyolefins (Figure 1).
Scheme 3. Scheme of hydrogenation of iso- and syndiotactic cis-1,4 poly(1,3-pentadiene) (iP(EP) and sP(EP)), and *cis*-1,4 poly(isoprene) (PI). **Reactions:** (A) diimide generation by thermal decomposition of TSH and (B) hydrogenation of unsaturated polymers with diimide.

Figure 1. FTIR spectra of (A) isotactic *cis*-1,4 poly(1,3-pentadiene) (top) and its saturated polymers (bottom), (B) syndiotactic *cis*-1,4 poly(1,3-pentadiene) (top) and its saturated polymers (bottom) and (C) *cis*-1,4 poly(isoprene) (top) and its saturated polymers (bottom).

Figure 2. $^1$H-NMR spectra (C$_2$D$_2$Cl$_4$, 103 °C, HMDS) of the unsaturated iP(EP) (a), sP(EP) (b) and (PI) (c), and saturated H-iP(EP) (d), H-sP(EP) (e) and H-PI (f).
The $^1$H-NMR spectra of sP(EP), iP(EP), PI and those of the corresponding hydrogenated products H-sP(EP), H-iP(EP) and H-PI, are shown in Figure 2. As it is clearly evident the peaks in the olefinic region (from 5.2 to 5.4 ppm), observed in the $^1$H-NMR spectra of the diene polymers, and due to the olefinic hydrogen atoms, are not observed in the $^1$H-NMR spectra of the hydrogenated polymers, confirming indeed the complete hydrogenation of the diene polymers.

The structure and tacticity of the resulting E/P copolymers were investigated by means of $^1$H and $^{13}$C-NMR, 2D NMR experiments [i.e., Heteronuclear Single Quantum Correlation (HSQC)] and X-ray diffraction analysis. Figure 3 shows the $^{13}$C-NMR spectra of the diene polymers; the peaks were assigned as already reported [39].

| polymer/ppm | C1   | C2   | C3   | C4   | C5   |
|------------|------|------|------|------|------|
| PI         | 30.44| 123.35| 133.30| 24.60| 21.38|
| sP(EP)     | 33.37| 124.62| 134.75| 30.31| 18.73|
| iP(EP)     | 33.38| 124.73| 134.72| 30.42| 18.84|

**Figure 3.** $^{13}$C-NMR spectra ($C_2D_2Cl_4$, 103 °C, HMDS) of the unsaturated polymer: (a) PI, (b) sP(EP) and (c) iP(EP).

The $^{13}$C-NMR spectra of the hydrogenated polymers (E/P copolymers) are shown in Figure 4 and exhibit four major resonances around 17.9 (C5), 22.6 (C2), 31.0 (C4), and 35.7 (C1,C3) ppm likely corresponding to the four unique signals of a perfectly alternating E/P copolymer structure. The chemical shifts are very close for the three hydrogenated polymers so that, on the basis of the $^{13}$C-NMR spectra only, it is not possible to distinguish the tacticity of the copolymers obtained with the hydrogenation reaction. In principle, however, since the hydrogenation reaction in the case of poly(1,3-pentadiene)s does not lead to the formation of new asymmetric carbon atoms, it is reasonable to assume that the tacticity of the diene polymer precursors is maintained in the alternating resulting E/P copolymers, that is isotactic for H-iP(EP) and syndiotactic for H-sP(EP). This assumption was
confirmed by means of the two-dimensional correlation spectroscopy, HSQC experiment, as the presence of a cross peak is indicative of protons and carbons directly linked through $^1J_{CH}$, and was able to give information about the different tacticity of the E/P copolymers. Results of these experiments are shown in Figure 5. Specifically, the signal at about 22.6 ppm, corresponding to the $\beta\beta$ methylene carbon, has proved to be diagnostic of the tacticity of the copolymer, as it is influenced by the arrangement of the methyl substituents, although not adjacent to the carbon atom bearing the methyl.

| Polymer/ppm | C1/C3 | C2  | C4  | C5  |
|------------|-------|-----|-----|-----|
| H-PI       | 35.72 | 22.60 | 30.96 | 17.92 |
|            | 35.69 | 22.59 | 30.96 | 17.88 |
|            | 35.66 | 22.59 | 30.98 | 17.84 |
|            | 35.63 | 22.59 | 30.98 | 17.92 |
| H-sP(EP)   | 35.69 | 22.61 | 30.96 | 17.82 |
| H-iP(EP)   | 35.66 | 22.59 | 30.98 | 17.92 |

In the HSQC spectrum of the product of the hydrogenation of isotactic cis-1,4 poly(1,3-pentadene) (Figure 5a, sP(EP)), the C2 carbon at $\delta = 22.59$ ppm correlates with two cross peaks at $\delta_{CH} = 1.25$ and 1.14 ppm, respectively. This is indicative of a methylene to which two magnetically non-equivalent protons are linked, as they display two different resonance frequencies “like in a different environment”, thus suggesting that the E/P copolymer obtained by hydrogenation of sP(EP) has an isotactic structure [40,41].

In the case of the E/P copolymer (Figure 5b) obtained by hydrogenation of sP(EP), the methylene at $\delta = 22.61$ ppm showed a single correlation peak at $\delta_{CH} = 1.19$ ppm, meaning a linking with two magnetic equivalent protons, in agreement with the syndiotactic structure of H-sP(EP). Finally, for the E/P copolymer obtained by hydrogenation of PI, the 2D HSQC experiment suggests the coexistence of isotactic and syndiotactic stereoregularities (Figure 5c). The syndiotacticity (associated to the single cross peak for $\delta_{C} = 22.6$ ppm, $\delta_{CH} = 1.19$ ppm) seems to be slightly preferred with respect to the isotacticy (two cross peaks for $\delta_{C} = 22.6$ ppm, $\delta_{CH} = 1.13$ and 1.27 ppm), being the single cross peak intensity more pronounced in the 2D spectrum. Once the tacticity was established, the peaks multiplicity observed for the $^{13}$C resonances in the $^{13}$C-NMR spectrum of H-PI (Figure 4, black line; 35.72, 35.69, 35.66, 35.63 ppm for C1/C3 carbons; 17.92, 17.88, 17.84 ppm for C5 carbon; some enlargement of the peaks at 22.60 and 30.96 ppm corresponding to carbons C2 and C4, respectively), could be reasonably related to the sensitivity of the carbon atoms up to triad level (in case of C5) and tetrads level (C1/C3 carbons).
The X-ray powder diffraction profiles of the hydrogenated polymers H-iP(EP), H-sP(EP), and H-PI are shown in Figure 6. It is apparent that all samples show broad diffraction profiles with an absence of Bragg reflections, indicating that all samples are amorphous. The diffraction profiles do not change upon thermal treatments and the samples do not crystallize even after annealing at relatively high temperatures or upon aging at room and low temperatures. Moreover, in the case of sample iP(EP), that can be stretched at relatively high deformations, crystallization does not take place by stretching up to high degrees of deformation and even keeping the sample under tension at low temperature for long time. The NMR data of Figures 4 and 5 as well as the diffraction data of Figure 6 indicate that the E/P alternating copolymers have a regular stereochemical structure, isotactic and syndiotactic for H-iP(EP) and H-sP(EP), respectively, and a statistical atactic structure for H-PI; the regular copolymers are however not able to crystallize.

The DSC heating curves of samples H-iP(EP), H-sP(EP) and H-PI are shown in Figure 7. According to the X-ray diffraction profiles of Figure 6, all DSC curves show only a glass transition at about −60 °C and the absence of any endothermic signal (Table 2). Only the glass transition at the same temperatures is observed in the successive cooling scans with absence of exothermic signals.
Figure 6. X-ray powder diffraction profiles of as-prepared samples of E/P alternating copolymers corresponding to the hydrogenated polymers H-iP(EP) (a), H-sP(EP) (b), and H-PI (c).

Figure 7. DSC heating curves, recorded at 10 °C/min, of as-prepared samples of alternating E/P copolymers corresponding to the hydrogenated polymers H-iP(EP) (a), H-sP(EP) (b), and H-PI (c).

Table 2. Values of average molecular mass ($M_w$), molecular weight distribution ($M_w/M_n$) and glass transition temperature ($T_g$) of the alternated E/P copolymers obtained by hydrogenation of the corresponding poly(1,3-diene).

| E/P Copolymers | Corresponding Poly(1,3-diene)     | $M_w$ $^1$ (×10$^{-3}$) | $M_w/M_n$$^1$ | $T_g$ $^2$ (°C) |
|----------------|----------------------------------|--------------------------|----------------|-----------------|
| H-iP(EP)       | isotactic cis-1,4 poly(1,3-pentadiene) | 194.8                    | 2.8            | −58             |
| H-sP(EP)       | syndiotactic cis-1,4-poly(1,3-pentadiene) | 60.5                     | 3.1            | −56             |
| H-PI           | cis-1,4 poly(isoprene)            | 249.3                    | 2.8            | −59             |

$^1$ determined by SEC; $^2$ determined by DSC.
The mechanical properties under tensile deformation of the three E/P alternating copolymers of different stereochemical structure have also been studied. The stress-strain curves recorded at room temperature of compression-molded films of the hydrogenated polymers are shown in Figure 8. According to the absence of crystallinity, all samples show low values of the Young modulus (0.6–1.0 MPa) and of the stress at any strain and viscous flow already at relatively low deformations. The differences in the stress-strain curves are mainly related to the different molecular masses of the three alternating copolymers. Higher values of the stress are, indeed, shown by the sample H-PI of higher molecular mass (Figure 8).

![Figure 8](image-url)  
Figure 8. Stress-strain curves recorded at room temperature of compression-molded films of alternating E/P copolymers corresponding to the hydrogenated polymers H-iP(EP), H-sP(EP), and H-PI. The dashed portions of the stress-strain curves indicate the deformation at which viscous flow without breaking occurs.

3. Materials and Methods

3.1. Materials

Manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere using a dual vacuum/nitrogen line and standard Schlenk-line techniques. Toluene (≥99.7% pure, Aldrich, Milano, Italy) and heptane (≥99% pure, Aldrich) were refluxed over Na for about 8 h and then distilled and stored over molecular sieves under nitrogen. o-Xylene (Aldrich, anhydrous grade), p-Toluenesulfonylhydrazide (TSH, Aldrich), deuterated solvent for NMR measurements (C₂D₂Cl₄) (Cambridge Isotope Laboratories, Inc., Tewksbury, MA, USA), diethylaluminum chloride (AlEt₂Cl) (97% pure Fluka-Aldrich, Milano, Italy), triisobutylaluminum (Al(Bu₃) (98% pure, Aldrich), methylaluminoxane (MAO) (10 wt% solution in toluene, Aldrich) and Nd(OCOC₇H₁₅)₃ (Strem Chemicals, Bischheim, France) were used as received. (E)-1,3-pentadiene (96% pure, Fluka) and isoprene (98%, Aldrich,) were refluxed over calcium hydride for about 4 h, then distilled trap-to-trap, and stored under nitrogen. Isotactic cis-1,4-poly(E-1,3-pentadiene) and cis-1,4 poly(isoprene) were synthesized with the catalyst AlEt₂Cl/(NdOCOC₇H₁₅)/AlBu₃ as described in reference 21 and 32/33, respectively; syndiotactic cis-1,4 poly(E-1,3-pentadiene) was synthesized with the catalyst CoCl₂(P⁵Bu₂Me)₂/MAO as described in [34].

3.2. Hydrogenation Procedure

The hydrogenation was carried out in a round-bottom flask equipped with a reflux condenser, a nitrogen inlet port, and a temperature controller. Typically, the specified amount of the diene polymer was dissolved in o-xylene. The mixture was continuously stirred at room temperature until the polymer
was completely dissolved. TSH was then added and the mixture was refluxed by slowly heating to 120 °C. After 3 days the mixture was allowed to cool spontaneously to room temperature and TSH was added. This operation is repeated once again. Upon completion of the reaction, the hydrogenated sample was hot-filtered, the volume of the filtered solution was reduced under vacuum, and the dissolved polymer precipitated with methanol and collected by filtration. The polymer was dried under vacuum at room temperature, and then it was extracted with acetone through a Soxhlet method for 10 h in order to remove any excess TSH and by products originating from TSH decomposition. The residual polymer was finally dried under vacuum, dissolved in toluene, precipitated into methanol, and dried again under vacuum at room temperature to constant weight. Specifically, for each polymer sample the conditions were:

3.2.1. Hydrogenation of Isotactic cis-1,4 poly(1,3-pentadiene)

Polymer 2.9 g; xylene, 300 mL; first addition of THS, 20.0 g (1.07 × 10⁻¹ mol); second and third addition of THS, 30.0 g (1.87 × 10⁻¹ mol).

3.2.2. Hydrogenation of Syndiotactic cis-1,4 poly(1,3-pentadiene)

Polymer 0.5 g; xylene, 70 mL; first addition of THS, 9.0 g (5.0 × 10⁻² mol); second and third addition of THS, 10.0 g (5.56 × 10⁻² mol).

3.2.3. Hydrogenation of cis-1,4 poly(isoprene)

Polymer 0.5 g; xylene, 100 mL; first addition of THS, 8.0 g (4.44 × 10⁻² mol); second and third addition of THS, 9.0 g (5.0 × 10⁻² mol).

3.3. Characterization

¹³C- and ¹H-NMR measurements were carried out on an Avance 400 spectrometer (Bruker, Milano, Italy) The spectra were obtained in C₂D₂Cl₄ at 103 °C (hexamethyldisiloxane, HMDS, as internal standard). The concentration of polymer solutions was about 10 wt %. ¹³C parameters were: spectral width 17 kHz; 90° pulse 11.0 μs PL1 − 5.0 dB, with a delay of 16 s. The 2D spectra were acquired on a Bruker DMX 600 MHz instrument, (14.1 T), at 330 K. The g-HSQC experiment, was performed by considering a coupling constant JCH = 130 Hz; data matrix 2 K × 256; number of scans128, 90° pulse calculated for each sample, PL1 − 2.2 dB. Molecular weight averages (M_w) and molecular weight distribution (M_w/M_n) were obtained by a high temperature GPCV2000 size exclusion chromatography (SEC) system (Waters, Milano, Italy) using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three PL Gel Olexis columns, o-dichlorobenzene as the mobile phase, 0.8 mL min⁻¹ flow rate, and 145 °C temperature. Universal calibration of the SEC system was performed using eighteen narrow M_w/M_n polystyrene standards with molar weights ranging from 162 to 5.6 × 10⁶ g mol⁻¹. For the analysis, about 12 mg of the polymer was dissolved in 5 mL of o-dichlorobenzene with 0.05% of BHT as the antioxidant.

X-ray powder diffraction profiles were obtained with Ni filtered CuKα radiation with an automatic diffractometer X-Pert by Panalytical (Westborough, MA, USA). Thermal analysis was performed with a DSC30/2285 differential scanning calorimeter (Mettler, Milano, Italy) equipped with a liquid nitrogen cooling system for measurements at low temperature. The scans were recorded in flowing nitrogen atmosphere at heating or cooling rates of 10 °C min⁻¹. Compression molded samples were prepared by heating the dry-precipitated powders at 120 °C for 10 min under a press at very low pressure and cooling to room temperature by circulating cold water inside the press plates.

Mechanical tests have been performed at room temperature on compression-molded films with a universal mechanical tester Zwicky by ZwickRoell (Genova, Italy), following the standard test method for tensile properties of thin plastic sheeting ASTM D882-83. 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 deformation ε = 100 × (L_f − L₀)/L₀, where L₀ 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. 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. The reported stress-strain curves and the values of the mechanical properties are averaged over at least five independent experiments.

4. Conclusions

Perfectly alternating ethylene/propylene copolymers having isotactic, syndiotactic and atactic structures have been obtained by means of hydrogenation of highly stereoregular isotactic cis-1,4 poly(1,3-pentadiene), syndiotactic cis-1,4 poly(1,3-pentadiene) and cis-1,4-poly(isoprene), respectively. The copolymers were fully characterized by NMR (1H, 13C and 2D), XRD, and their thermal and mechanical properties were investigated. Despite their high stereoregularity, as clearly evidenced by the NMR analysis, all the copolymers were found to be amorphous, exhibiting low mechanical properties.

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References

1. Kravchenko, R.; Waymouth, R.M. Ethylene-propylene copolymerization with 2-arylindene zirconocenes. Macromolecules 1998, 31, 1–6. [CrossRef]
2. D’Orazio, L.; Mancarella, C.; Martuscelli, E.; Sticotti, G.; Massari, P. Melt rheology, phase structure and impact properties of injection-moulded samples of isotactic polypropylene/ethylene-propylene copolymer (iPP/EPR) blends: Influence of molecular structure of EPR copolymers. Polymer 1993, 34, 3671–3676. [CrossRef]
3. Kaminsky, W. Trends in Polyolefin Chemistry. Macromol. Chem. Phys. 2008, 209, 459–466. [CrossRef]
4. Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. Selectivity in propene polymerization with metallocene catalysts. Chem. Rev. 2000, 100, 1253–1345. [CrossRef] [PubMed]
5. Ittel, S.D.; Johnson, L.K.; Brookhart, M. Late-Metal Catalysts for Ethylene Homo- and Copolymerization. Chem. Rev. 2000, 100, 1169–1203. [CrossRef] [PubMed]
6. Fan, W.; Waymouth, R.M. Alternating copolymerization of ethylene and propylene: Evidence for selective chain transfer to ethylene. Macromolecules 2001, 34, 8619–8625. [CrossRef]
7. Leclerc, M.K.; Waymouth, R.M. Alternating ethene/propene copolymerization with a metallocene catalyst. Angew. Chem. Int. Ed. 1998, 37, 922–925. [CrossRef]
8. Jin, J.; Uozumi, T.; Sano, T.; Teranishi, T.; Soga, K.; Shiono, T. Alternating copolymerization of ethylene and propene with the [ethylene(1-indenyl)(9-fluorenyl)]zirconium dichloride-methylaluminoxane catalyst system. Macromol. Rapid. Commun. 1998, 19, 337–339. [CrossRef]
9. Rose, J.M.; Cherian, A.E.; Coates, G.W. Living polymerization of α-olefins with an α-Diimine Ni(II) catalyst: Formation of well-defined ethylene−propylene copolymers through controlled chain-walking. J. Am. Chem. Soc. 2006, 128, 4186–4187. [CrossRef] [PubMed]
10. Ricci, G.; Sommazzi, A.; Masi, F.; Ricci, M.; Boglia, A.; Leone, G. Well-defined transition metal complexes with phosphorus and nitrogen ligands for 1,3-dienes polymerization. Coord. Chem. Rev. 2010, 254, 661–676. [CrossRef]
11. Ricci, G.; Morganti, D.; Sommazzi, A.; Santi, R.; Masi, F. Polymerization of 1,3-dienes with iron complexes based catalysts. Influence of the ligand on catalyst activity and stereospecificity. J. Mol. Cat A: Chem. 2003, 204/205, 287–293. [CrossRef]
12. Ricci, G.; Battistella, M.; Porri, L. Chemoselectivity and stereoselectivity of chromium (II) catalysts for 1,3-diene polymerization. *Macromolecules* **2001**, *34*, 5766–5769. [CrossRef]

13. Ricci, G.; Italia, S.; Giarrusso, A.; Porri, L. Polymerization of 1,3-dienes with the soluble catalyst system methylaluminoxanes-[CpTiCl3]. Influence of monomer structure on polymerization stereoselectivity. *J. Organomet. Chem.* **1993**, *451*, 67–72. [CrossRef]

14. Leone, G.; Boccia, A.C.; Ricci, G.; Giarrusso, A.; Porri, L. Polymerization of (E)-1,3-pentadiene and (E)-2-methyl-1,3-pentadiene with neodymium catalysts: Examination of the factors that affect the stereoselectivity. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 3227–3232. [CrossRef]

15. Boccia, A.C.; Leone, G.; Boglia, A.; Ricci, G. Novel stereoregular cis-1,4 and trans-1,2 poly(diene)s: Synthesis, characterization, and mechanistic considerations. *Polymer* **2013**, *54*, 3492–3503. [CrossRef]

16. Ricci, G.; Leone, G.; Boglia, A.; Bertini, F.; Boccia, A.C.; Zetta, L. Synthesis and characterization of isotactic 1,2-Poly(E-3-methyl-1,3-pentadiene). Some remarks about the influence of monomer structure on polymerization stereoselectivity. *Macromolecules* **2009**, *42*, 3048–3056. [CrossRef]

17. Ricci, G.; Leone, G.; Boglia, A.; Boccia, A.C.; Zetta, L. cis-1,4-alt-3,4 Polysoprene: Synthesis and characterization. *Macromolecules* **2009**, *42*, 9263–9267. [CrossRef]

18. Pirozzi, B.; Napolitano, R.; Giusto, G.; Ricci, G. Determination of the crystal structure of isotactic cis-1,4 Poly(1,3-hexadiene) by X-Ray Diffraction and molecular mechanics. *Macromol. Chem. Phys.* **2008**, *209*, 1012–1020. [CrossRef]

19. Pirozzi, B.; Napolitano, R.; Giusto, G.; Esposito, S.; Ricci, G. Determination of the crystal structure of syndiotactic 1,2-poly(E-3-methyl-1,3-pentadiene) by X-ray diffraction and molecular mechanics. *Macromolecules* **2007**, *40*, 8962–8968. [CrossRef]

20. Ricci, G.; Boglia, A.; Motta, T.; Bertini, F.; Boccia, A.C.; Zetta, L.; Alberti, E.; Fanulari, A.; Arosio, P.; Meille, S.V. Synthesis and structural characterization of syndiotactic trans-1,2 and cis-1,2 polyhexadienes. *J. Polym. Sci Part A: Polym. Chem.* **2007**, *45*, 5339–5353. [CrossRef]

21. Ricci, G.; Motta, T.; Boglia, A.; Alberti, E.; Zetta, L.; Bertini, F.; Arosio, P.; Fanulari, A.; Meille, S.V. Synthesis, characterization, and crystalline structure of syndiotactic 1,2-polypentadiene: The cis polymer. *Macromolecules* **2005**, *38*, 8345–8352. [CrossRef]

22. Ricci, G.; Alberti, E.; Zetta, L.; Motta, T.; Bertini, F.; Mendichi, R.; Arosio, P.; Fanulari, A.; Meille, S.V. Synthesis, characterization and molecular conformation of syndiotactic 1,2 polypentadiene: The trans polymer. *Macromolecules* **2005**, *38*, 8353–8365. [CrossRef]

23. Purevsuren, B.; Allegra, G.; Meille, S.V.; Farina, A.; Porri, L.; Ricci, G. cis-Isotactic 1,4-polypentadiene. NMR solution characterization and crystal structure of polymers prepared with neodymium-catalytic systems. *Polymer J.* **1998**, *30*, 431–443. [CrossRef]

24. Meille, S.V.; Capelli, S.; Ricci, G. Structural characterization of syndiotactic 1,2-poly(4-methyl-1,3-pentadiene). *Macromol. Rapid Commun.* **1995**, *16*, 891–897. [CrossRef]

25. Meille, S.V.; Capelli, S.; Allegro, G.; Ricci, G. Isotactic cis-1,4-poly(3-methyl-1,3-pentadiene): A new conformation for isotactic cis-1,4-polydienes. *Macromol. Rapid Commun.* **1995**, *16*, 329–335. [CrossRef]

26. Ricci, G.; Italia, S.; Porri, L. Polymerization of (Z)-1,3-pentadiene with CpTiCl3/MAO. Effect of temperature on polymer structure and mechanistic implications. *Macromolecules* **1994**, *27*, 868–869. [CrossRef]

27. Cabassi, F.; Porzio, W.; Ricci, G.; Bruckner, S.; Meille, S.V.; Porri, L. Structural studies on 1,4-cis-poly(2-methyl-1,3-pentadiene) synthesized with Nd catalysts. *Makromol. Chem.* **1988**, *189*, 2135–2143. [CrossRef]

28. Bruckner, S.; Meille, S.V.; Porzio, W.; Ricci, G. The structure of one crystalline form of isotactic 1,4-cis-poly(2-methyl-1,3-pentadiene). An application of the rietveld method. *Macromol. Chem.* **1988**, *189*, 2145–2152. [CrossRef]

29. De Rosa, C.; Auricamma, F.; Santillo, C.; Di Girolamo, R.; Leone, G.; Ricci, G. Chirality, entropy and crystallization in polymers: Isotactic poly(3-methyl-1-pentene) as an example of influence of chirality and entropy on the crystal structure. *CrystEngComm.* **2015**, *17*, 6006–6013. [CrossRef]

30. De Rosa, C.; Auricamma, F.; Santillo, C.; Di Girolamo, R.; Leone, G.; Boccia, A.C.; Ricci, G. Crystal structure of isotactic poly((R,S)-3-methyl-1-pentene). *Macromolecules* **2015**, *48*, 5251–5266. [CrossRef]

31. Ricci, G.; Leone, G.; Boccia, A.C.; Pierro, I.; Zanchin, G.; Mauri, M.; Scoti, M.; Malafronte, A.; Auricamma, F.; De Rosa, C. Perfectly alternating ethylene/2-butene copolymers by hydrogenation of highly stereoregular 1,4-Poly(1,3-diene)s: Synthesis and characterization. *Macromolecules* **2017**, *50*, 754–761. [CrossRef]
32. Ricci, G.; Boffa, G.; Porri, L. Polymerization of 1,3-dialkenes with neodymium catalysts. Some remarks on the influence of the solvent. Makromol. Chem. Rapid Commun. 1986, 7, 355–359. [CrossRef]
33. Ricci, G.; Italia, S.; Cabassi, F.; Porri, L. Neodymium catalysts for 1,3-diene polymerization: Influence of the preparation conditions on activity. Polymer Commun. 1987, 28, 223–226.
34. Ricci, G.; Forni, A.; Boglia, A.; Motta, T. Synthesis, structure, and butadiene polymerization behavior of alkylphosphine cobalt(II) complexes. J. Mol. Catal. A: Chem. 2005, 226, 235–241. [CrossRef]
35. Wang, H.; Yang, L.; Rempel, G.L. Homogeneous hydrogenation art of nitrile butadiene rubber: A review. Polym. Rev. 2013, 53, 192–239. [CrossRef]
36. Santin, C.K.; Jacobi, M.M.; Schuster, R.H. Influence of 1,2 units content on the hydrogenation of polydienes by TSH. J. Appl. Polym. Sci. 2011, 119, 1195–1203. [CrossRef]
37. Samran, J.; Phinyocheep, P.; Daniel, P.; Kittipoom, S. Hydrogenation of unsaturated rubbers using diimide as a reducing agent. J. Appl. Polym. Sci. 2005, 95, 16–27. [CrossRef]
38. Mango, L.A.; Lenz, R.W. Hydrogenation of unsaturated polymers with diimide. Makromol. Chem. 1973, 163, 13–36. [CrossRef]
39. Zetta, L.; Gatti, G.; Audisio, G. Long-range steric effects on C-13 chemical-shift of hydrocarbon polymers. Macromolecules 1978, 11, 763–766. [CrossRef]
40. Busico, V.; Cipullo, R. Microstructure of polypropylene. Prog. Polym. Sci. 2001, 26, 443–533. [CrossRef]
41. Markova, N.; Ivanova, G.; Enchev, V.; Simeonova, M. Tacticity of poly(butyl-α-cyanoacrylate) chains in nanoparticles: NMR spectroscopy and DFT calculations. Struct. Chem. 2012, 23, 815–824. [CrossRef]

Sample Availability: Samples of the Alternating Ethylene/Propylene Copolymers are available from the authors.