New Stereoregularity in the Stereospecific Polymerization of Bulky Strained Olefins: Diheterotactic Polynorbornene

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ABSTRACT: A new semicrystalline polynorbornene was obtained by stereospecific polymerization with $CrCl_2$(dppa)−MAO catalyst (dppa = bis(diphenylphosphino)amine). NMR, X-ray diffraction, and modeling techniques were used, concentrating on the soluble lower molecular weight fractions, to characterize the polymer structure. The polymer presents a 2,3-*exo*-diheterotactic stereochemistry never observed before in the polymerization of alkenes. High symmetry, low energy chain conformations accounting for ^{13}C NMR data are devised. Efficient crystalline packing models consistent with powder X-ray diffraction patterns and density requirements are proposed.

Introduction

The polymerization of strained and bulky cyclic olefins, also using catalysts which are known to be stereospecific, generally affords polymers that are amorphous. It is often unclear whether this is the result of the conformational rigidity and the steric strain of the resulting polymers or if it is due to insufficient stereospecificity of the polymerization process. Indeed, the stereochemistry of the synthesized polymers is usually difficult to establish with certainty.

In the specific case of norbornene, substantial efforts were devoted to devise catalysts for vinyl polymerization, to obtain completely saturated polymers retaining the bicyclic structural unit: a review on this topic has recently appeared.[1] Most investigations were carried out with catalysts based on Ni and on Zr; nevertheless, catalysts based on Ti, Cr, Co, and Pd have also been examined. In general polymers exhibiting low crystallinity and high molecular weight that were characterized by a rather low solubility were obtained, making their structural characterization difficult and hardly devoid of ambiguities. No reports exist in the literature concerning highly stereoregular vinyl-type polynorbornenes (e.g., diisotactic, disyndiotactic). Only the synthesis and the crystal structure of a disyndiotactic oligomer (heptamer)[2] and of a polymer having a regular structure resulting from combined vinylic insertion and σ-bond metathesis[3] have been described. Predominantly isotactic polymers and polymers with a very low isotactic content (mixtures of *rr* and *mr* triads) were reported,[4] but their characterization, essentially by NMR, may be not very accurate, mainly due to the substantial irregularity of the polymers.

Narrowing the field to norbornene polymerization with Cr catalysts, we are aware of two papers by Heitz[5] concerning $[CpCrMeCl]_2$−MAO (Cp = C_5H_5, C_5Me_5, Ind, Flu) systems leading to partially crystalline polymers, while a more recent contribution by Bochmann[6] reports on the polymerization with catalysts based on chromium(II) allyl ($Cr[1,3\text{-}C_3H_3(SiMe_3)_2]_2$) and chromium(IV) alkyl ($Cr(CH_2SiMe_3)_4$ complexes giving, respectively, an insoluble vinyl-type polynorbornene and oligomers.

In the present investigation, we report the polymerization of norbornene with the catalyst obtained combining methylaluminoxane (MAO) with $CrCl_2$(dppa) (dppa = bis(diphenylphosphino)amine), a system found to be highly active and stereospecific in the polymerization of butadiene to yield a 1,2-syndiotactic polymer.[7] The polynorbornene we obtained shows, after fractionation, a significant crystallinity. Using a combination of NMR, X-ray diffraction, and molecular modeling approaches, we were able to establish that the stereochemistry of the polynorbornene we synthesized is largely diheterotactic. In previous work on polynorbornenes, the possibility of this type of stereoregularity was never taken into consideration. Indeed, as far as we know, we are reporting the first example of a diheterotactic polyolefin obtained by means of stereospecific polymerization.

Experimental Section

Materials. $CrCl_2$(dppa) was prepared according to the experimental procedure already reported in the literature.[7] Methylaluminoxane (MAO) (Crompton, 10 wt % solution in toluene) was used as received. MAO without free-$Al(CH_3)_3$ was prepared removing toluene and unreacted trimethylaluminum from the commercial solution under vacuum, washing the residue with pentane, and drying under vacuum at room temperature for one night. Toluene (Fluka, > 99.5% pure) was refluxed over Na for ca. 8 h and then distilled and stored over molecular sieves under dry nitrogen. Norbornene (Aldrich, 99% pure) was stirred over molten potassium at 80 °C under dry nitrogen for 4 h and then distilled.

Polymerization of Norbornene. All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk line techniques. Norbornene polymerizations were carried out as follows: a toluene solution of the monomer was transferred into the reactor vessel; the solution was brought to the desired polymerization temperature, then methylaluminoxane and the chromium compound, both as toluene solutions, were added in the order. Polymerizations were stopped with methanol containing a small amount of hydrochloric acid; the precipitated polymers were filtered, repeatedly washed with fresh methanol, and then dried in vacuum to constant weight.

Polymer Characterization. ^{13}C and ^1H NMR measurements were carried out on Bruker Avance 400 spectrometers. The spectra were obtained in $C_2D_2Cl_4$ at different temperatures (50, 80, 103, and 120 °C) using hexamethyldisiloxane, HMDS, as internal standard. The concentration of the polymer solutions was about 10 wt %. Differential scanning calorimetry (DSC) scans were carried out on a Perkin-Elmer Pyris 1 instrument. Typically, ca. 10 mg of

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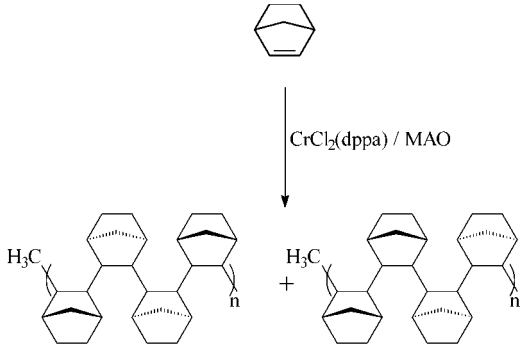
Table 1. Polymerization of Norbornene with $CrCl_2$(dppa)−MAO[a]

run	T (°C)	time (min)	yield (g)	N^b	$M_w{}^c$ (g mol^{-1})	$M_w/M_n{}^c$	$T_g{}^d$ (°C)
1	+20	10	1.24	24840	1305	1.7	95
2	−30	1320	1.34	203	2760	1.4	133
3[e]	+20	80	1.66	2070	*f*	*f*	*g*

[a] Polymerization conditions: toluene (total volume, 18 mL); norbornene, 2.45 g as toluene solution; MAO, Al/Cr = 1000; Cr, 5×10^{-6} mol. [b] Mass (g) of polymer obtained per mol of Cr per min. [c] Determined by GPC analysis. [d] Determined by DSC analysis. [e] MAO, without free-$Al(CH_3)_3$, was used instead of commercial MAO. [f] The polymer is practically insoluble. [g] Not detected.

Scheme 1. Scheme of Formation of 2,3-*exo*-Diheterotactic Polynorbornene[a]



I **II**

[a] The repeat units (**I** and **II**) and possible different chain ends are shown.

polymer were analyzed in each run, with a scan speed of 20K/min under a dry nitrogen atmosphere. The molecular weight averages (M_w) and the molecular weight distribution (M_w/M_n) were obtained by a high temperature GPCV 2000 system (from Waters) using two online detectors: a differential viscometer and a refractometer. The experimental conditions consisted of three Olefi PSS columns, *o*-dichlorobenzene as the mobile phase, 0.8 mL/min flow rate, and 145 °C temperature. The calibration of the GPC system was constructed using eighteen narrow MWD polystyrene standards with molar masses ranging from 162 to 3.3×10^6 g/mol.

X-ray powder diffraction patterns (Cu Kα) were recorded in reflection mode using an Italstructure θ/θ diffractometer and in transmission with a Bruker P4 diffractometer equipped with a Hi-Star 2D detector. A sample mounted on a glass fiber was employed in the latter case (sample to detector distance of about 10 cm).

Molecular modeling involved both molecular mechanics (MM) and semiempirical quantum mechanics (QM) investigations. MM calculations were performed adopting the COMPASS forcefield[8] as implemented into the Forcite module of the Material Studio suite of programs.[9] Isolated infinite chain and packing models were investigated with and without symmetry constrains. Selected AM1 semiempirical calculations on isolated chain models were performed using the GAMESS-US package.[10]

Results and Discussion

Polymer Synthesis, Fractionation, and Thermal Analysis. The results of the polymerizations carried out at +20 and −30 °C with $CrCl_2$(dppa)−MAO are shown in Table 1 (runs 1 and 2, respectively); fully saturated vinyl addition polymers were obtained (see Scheme 1), as indicated by the fact that in the olefinic region of their ^{1}H spectra (Figure 1) no signals were observed. This evidence was confirmed by the absence of bands in the 1680−1620 cm^{-1} region in the IR spectra of the polymers.[6]

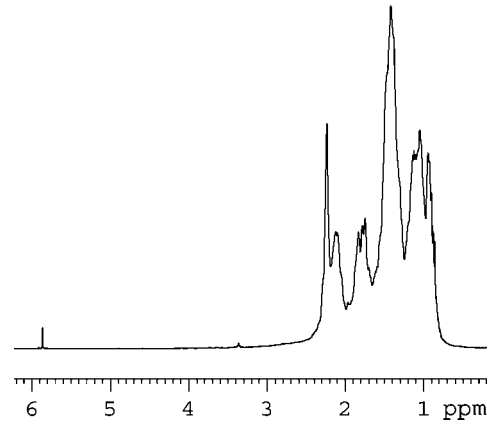


Figure 1. ^{1}H NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of polynorbornene (crude polymer) obtained with $CrCl_2$(dppa)−MAO at +20 °C.

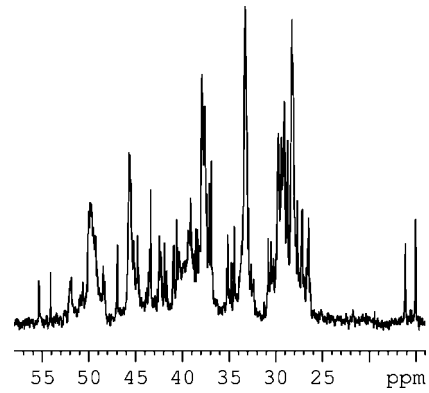


Figure 2. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of polynorbornene (crude polymer) obtained with $CrCl_2$(dppa)−MAO at +20 °C.

The polymerization carried out at 20 °C was extremely fast, yielding high conversion in a few minutes. Similar conversions could also be obtained at −30 °C, although with much longer polymerization times. The crude polymer molar masses, determined by GPC analyses, were found to be in general rather low (in the range 1000−3000 g mol^{-1}), consistent with the fact that in ^{13}C NMR spectra (Figure 2) signals corresponding to methyl end-groups (at 15.1 and 16.1 ppm), plausibly arising from norbornene insertion into Cr−Me bonds followed by rapid transfer to aluminum,[6] were observed. The GPC molecular weights are in good agreement with those deduced from the ^{13}C NMR spectra of the crude polynorbornenes obtained at +20 °C (Figure 2) and at −30 °C (spectrum not shown), applying the following equation:

$$n = A_{\Sigma C}/7A_{CH_3}$$

Here n is the degree of polymerization; A_{CH_3} is the integrated area of the signals corresponding to the methyl carbons around 15−16 ppm; $A_{\Sigma C}/7$ is sum of the integrated areas of all the other peaks observed in the spectrum divided by 7, i.e., by the number of carbon atoms in each norbornene monomer unit. The values of n obtained for the polymers synthesized at +20 and at −30 °C are around 10 and 19, respectively.

The extremely low molar masses of the polymers obtained are most probably a consequence of the transfer reaction to aluminum; this hypothesis is supported by the fact that when MAO without free-$Al(CH_3)_3$ is used instead of commercial MAO (10 wt % solution in toluene, containing free-$Al(CH_3)_3$ (Table 1, run 3)) an insoluble polymer is produced, most likely suggesting that a high molecular weight polymer has been

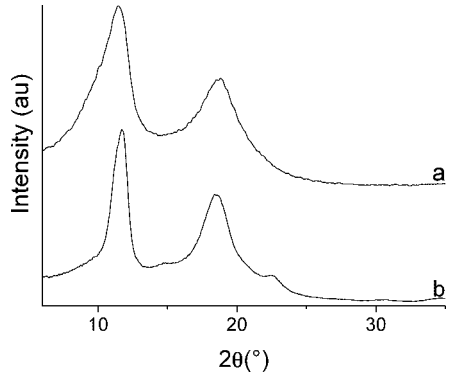


Figure 3. Experimental X-ray diffraction patterns: (a) the insoluble diheterotactic polynorbornene obtained employing $Al(CH_3)_3$-free methylaluminoxane (Table 1, run 3) and (b) the heptane insoluble fraction (see Table 2) of the polynorbornene obtained at −30 °C (Table 1, run 2).

Table 2. Results of the Fractionation of the Polynorbornene Obtained with $CrCl_2$(dppa)–MAO at −30 °C

polymer fraction	wt %	M_w[a] (g mol^{-1})	M_w/M_n[a]
heptane soluble	64.5	1950	1.3
heptane insoluble	35.5	4300	1.8

[a] Determined by GPC analysis.

formed. In the present investigation we decided to focus essentially on the soluble polymers obtained with commercial MAO as received, because of the clear need to characterize our materials and polynorbonenes in general by solution NMR spectroscopy. Use of MAO without free-$Al(CH_3)_3$ can be considered indeed a way for suppressing the transfer reaction and increasing the polymer molecular weight.

Polymer molecular weights were higher at low polymerization temperature, implying that the transfer reaction to the aluminum compound is increasingly disfavored with respect to the insertion reaction as the polymerization temperature decreases. The polymer obtained at −30 °C was extracted in continuous boiling heptane for about 24 h, allowing isolation of two different polymer fractions (Table 2).

Whereas the crude lower molecular weight polymers are amorphous, the heptane insoluble fraction shows considerable cristallinity by wide-angle X-ray diffraction. The diffraction pattern resulting from the unfractionated, insoluble polymer obtained with $Al(CH_3)_3$-free-MAO (Table 1, run 3), is shown in Figure 3a. Granting the substantially larger width of the diffraction maxima, the pattern of the insoluble polymer shows close correspondence, in the main peak positions and relative intensities, to the diffraction profile of the heptane insoluble fraction of the polymer obtained using commercial MAO (Figure 3b), indicating that the low molecular weight polymer obtained at −30 °C and the insoluble high molecular weight polymer obtained at 20 °C are likely to exhibit a similar type of stereoregularity.

The synthesized polymers (crude polymers, soluble and insoluble polymer fractions) were also characterized by thermal analysis. In the DSC scans (not shown) of the crude polymers (Table 1) and of the polymeric fractions (soluble and insoluble; see Table 2) no melting transition was detected up to 350 °C. Above this temperature, significant polymer decomposition was observed, implying that the melting points of the crystalline components are higher than the decomposition temperatures. This fact is not unexpected considering that the syndiotactic heptamer[2] shows a melting point of about 267 °C.

Consistent with the crystallinity observed by X-ray diffraction, it was not possible to evidence the glass transition temperature in the case of the insoluble fraction (residue to heptane

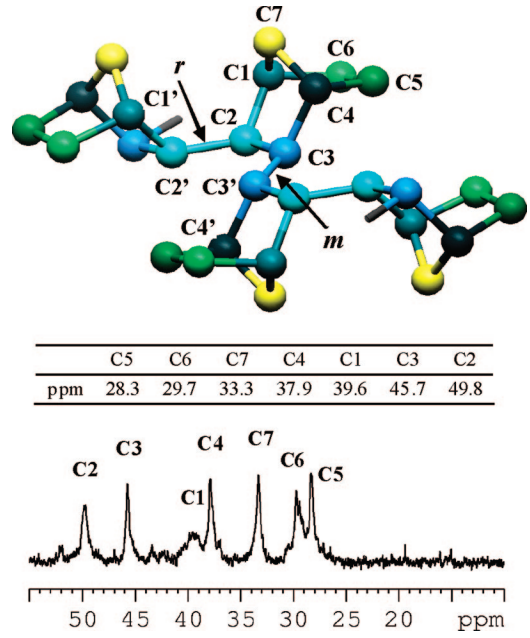


Figure 4. ^{13}C NMR spectrum ($C_2D_2Cl_4$, HMDS as internal standard, 103 °C) of the heptane insoluble fraction of the polynorbornene obtained with $CrCl_2$(dppa)−MAO at −30 °C. The structure and numbering scheme of 2,3-*exo*-diheterotactic polynorbornene are also shown: magnetically equivalent carbons have the same color. Main-chain bonds across *r* and *m* diads are indicated while hydrogens are omitted.

extraction, Table 2) and of the high molecular weight polymer obtained with $Al(CH_3)_3$-free MAO (Table 1, run 3). Two clearly different T_g values were instead observed for the crude polymers obtained at +20 and −30 °C (see Table 1), plausibly resulting from the different plasticizing action of lower molecular weights and of species containing variable amounts and types of stereoerrors. This hypothesis is supported also by the observation that soluble polymer fractions, obtained by extracting polymer samples with different boiling solvents (acetone, diethyl ether, heptane, toluene), exhibited glass transition temperatures increasing in the order acetone < diethyl ether < heptane < toluene, corresponding to the order of increasing molecular weight. We already mentioned that the T_g values of various polymers could also be affected by differences in stereoregularity, which may substantially influence local chain rigidity. We are however at the moment not able to further substantiate this hypothesis, because of the complexity of the crude polymers NMR spectra (see below), to be ascribed, at least in part, to the presence of a large number of terminal units signals.

NMR Characterization. The residue to heptane extraction of the polynorbornene obtained at −30 °C (Table 2), exhibiting a higher molecular weight with respect to the crude polymer, as indicated by the GPC analyses and by the lower intensities of chain end signals (around 15−16 ppm) in the ^{13}C NMR spectrum (Figure 4), was investigated carefully by NMR spectroscopy in order to determine the polymer microstructure.

Quite surprisingly, the ^{13}C NMR spectrum (Figure 4) shows essentially seven different peaks of nearly equal area, corresponding to the seven carbon atoms of a norbornene unit (see Figure 4); some additional minor intensity peaks are also observed, probably due to terminal units. Specifically, the sharpest resonances, at 29.7, 33.3, 37.9, and 45.7 ppm, persuasively suggest a stereoregular structure for the polymer under investigation. This indication is consistent with the diffraction pattern of the heptane insoluble fraction (Figure 3b) evidencing remarkable crystallinity: while diffraction maxima are few and relatively broad, the peak at $2\theta = 11.70°$ is quite sharp, suggesting that the broadness of the other maxima may

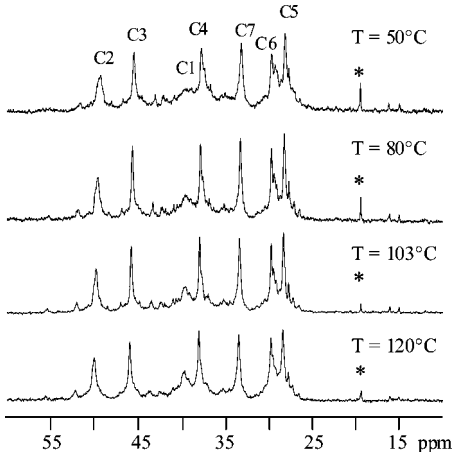


Figure 5. ^{13}C NMR spectra ($C_2D_2Cl_4$, HMDS internal standard) of 2,3-*exo*-diheterotactic polynorbornene recorded at 50, 80, 103, and 120 °C. An asterisk indicates the methyl signal of toluene impurity.

be due to overlapping peaks. ^{13}C NMR peak multiplicity was assigned with DEPT experiments: methylene carbons at 28.3, 29.7, and 33.3 ppm gave negative peaks while methyne carbons at 37.9, 39.6, 45.7, and 49.8 ppm gave positive peaks. Reference to polynorbornenes,[4] to norbornene hydrotrimers,[11] and to results by Wu and Lu (C1/C4 at 38.8 ppm in the *mm* triad, and at 41.3 ppm in the *rr* triad)[12] allowed assignments of the ^{13}C signals reported in Figure 4. The absence of signals in the 20−24 ppm region indicates that the polymer is *exo*-enchained.[13] The ^{13}C spectral data can be interpreted in a simple, straightforward manner, assuming a stereoregular 2,3-*exo*-diheterotactic[14,15] structure characterized by the regular repetition of (*mr*) triads. The structure of the polymer is shown in Scheme 1; we have reported the two possible repeat units, which have however the same structure, since the diad formed by the first two inserted monomer units can be isotactic or syndiotactic, as suggested by the fact that we always observe two different signals, having the same area, for the terminal methyl group. This stereochemistry is compatible with an idealized conformation, with a center of symmetry at the midpoint of rigorously trans C3−C3′ bonds at the center of *m* diads, and a 2-fold axis, orthogonal to the chain axis, through the midpoint of less constrained C2−C2′ bonds between monomers in *r* diads. As apparent in Figure 4, the asymmetric unit of this idealized model consists of a single norbornene while each carbon of the C1/C4, C2/C3, and C5/C6 pairs monitors a conformationally and magnetically different environment. The 4 ppm separation of the C2 and C3 peaks, at 49.8 and 45.7 ppm respectively, suggests that C3 could possibly be shielded by an additional γ-gauche effect. The C1 and C4 peaks, at 39.6 and 37.9 ppm, respectively, are separated by 1.7 ppm, and C1 is broadened over 4 ppm. This spectral feature suggests that while for the *m* diad the trans conformation of torsion angle C4−C3−C3′−C4′ is strongly preferred, the C1−C2−C2′−C1′ angle in the *r* diad can adopt various values with different γ-gauche effects on C1 and C1′, causing a 4 ppm spread for their chemical shifts. Similar signal splitting and broadening were observed but not discussed in ^{13}C spectra of a polynorbornene supposedly of low diisotacticity, but most likely consisting of *mr* sequences and small amounts of *rr* sequences.[4]

The ^{13}C NMR spectra of diheterotactic polynorbornene recorded at different temperatures (50, 80, 103 and 120 °C, Figure 5) seem to support the above interpretation. In fact, by increasing the temperature, it is possible to observe chemical shift variations for the C1, C2, C2′, and C1′ resonances, probably due to a rapid reorientation and interconversions among conformers, while the C4, C3, C3′, and C4′ resonances are unaffected by temperature variations indicating a low degree of mobility for this chain region due to a strongly preferred value for torsion angle C4−C3−C3′−C4′. These observations provide indeed strong and direct evidence that broadened resonances originate from different conformers and are associated with the conformational interconversion.

Molecular Modeling and Crystal Structure Analysis. The above interpretation of NMR data is confirmed by modeling and diffraction investigations. Low energy polynorbornene conformations can be built with a stereoregular 2,3-*exo*-diheterotactic stereochemistry and a chain repeat containing four monomers. On the contrary, low energy stereoregular 2,3-*exo*-diisotactic polynorbornenes with periodic conformations, even with more than one norbornene in the conformational repeat unit, have never been devised. Also the crystal structure of a stereoregular heptamer with 2,3-*exo*-disyndiotactic stereochemistry[2] displays no regularity in the torsion angle sequence. The idealized 2,3-*exo*-diheterotactic conformation is highly symmetric: the asymmetric unit consists of a single norbornene monomer and the chain shows *tci* line repetition group symmetry, i.e. *p*2/*c* rod group symmetry.[16] Exploration by molecular mechanics (MM) of the energy surface of the isolated infinite chain as a function of the chain periodicity assuming the mentioned symmetry, shows two shallow conformational minima at about 8.3 and 9.5 Å. As a consequence of the inversion center at the midpoint of the C3−C3′ bond, the two structures share a rigorously trans conformation of the torsion angle around this bond, i.e., across norbornene units within *m* diads. The two minimum-energy conformations differ for the C3−C2−C2′−C3′ torsion angle values, across monomer units in *r* diads, which are respectively about 120 and 170°. Indeed these two values are close to relative minima for racemic dimers whereas the conformational energy minimum for *meso*-norbornene dimers[17] is trans. The more extended backbone is energetically disfavored by about 1 kcal (mol monomer units)$^{-1}$ and chain symmetry relaxation does not significantly alter the two conformations. These results, which are in remarkable agreement with ^{13}C NMR suggestions, were confirmed by AM1 semiempirical calculations on chain models of 12 monomer units which show calculated periodicities, geometrical parameters and relative energies consistent with molecular mechanics. Both isolated chain models were used as starting points for the investigation of the crystalline structure, taking into account the limited but very valuable diffraction information. One chain unit cells preserving the full chain symmetry, i.e., in space group *P*2/*c*, were investigated first. Encouraging results were obtained in both cases but packing energy minimization and the fit with the diffraction data require to consider more complex models. With the more extended chain, i.e with both the *r* and *m* diads torsion angle trans, the best results were obtained for a model in space group *C*2/*c*, with lattice parameters $a = 11.04$ Å, $b = 11.41$ Å, c (chain repeat) $= 9.66$ Å, $\tau = 117.1°$ (Figure 6, dotted cell) with a calculated density of 1.153 Mg m^{-3} to be compared with an experimental value of 1.06 Mg m^{-3}. This structure coincides in essence with the absolute packing energy minimum we were able to determine. Rigid body refinement of this model with the Rietveld procedure,[18] gives a good fit to the observed diffraction pattern, as apparent in Figure 7. The primitive triclinic cell of the *C*2/*c* structure is also outlined in Figure 6: further refinement of the structure relaxing the 2/*c* symmetry might possibly explain the small inconsistencies between the calculated and the observed diffraction pattern. All the refined models suggest small crystal dimensions along the *c* axis, typically around 30 Å, corresponding to 10−15 monomer units, implying that the crystallizing stereoregular sequences are relatively short. With the 8.3 Å chain periodicity, i.e., with a 120° torsion angle across the *r* diad, packed models preserving the 2/*c* chain symmetry show slightly higher energy (ca. 2 kcal mol^{-1} of monomer units) and give a worse fit to the diffraction data.

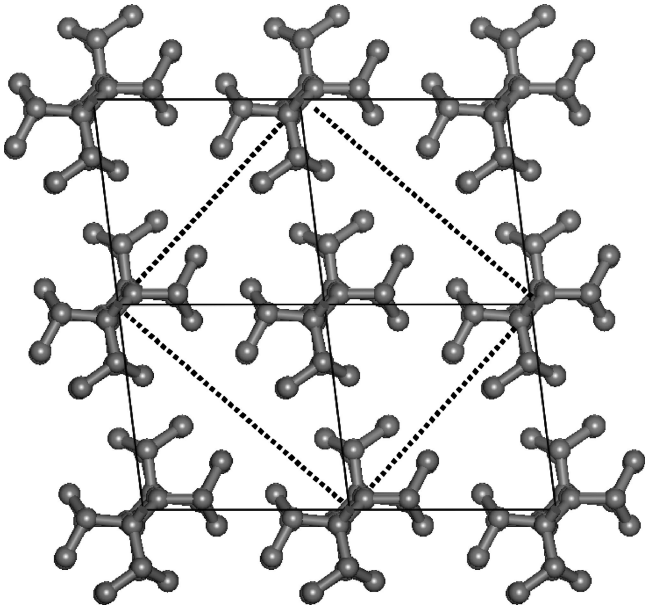


Figure 6. Projection along the chain axis of the refined packing model of 2,3-*exo*-diheterotactic polynorbornene. The centered monoclinic (dotted line) and the primitive triclinic (continuous line) lattices are shown.

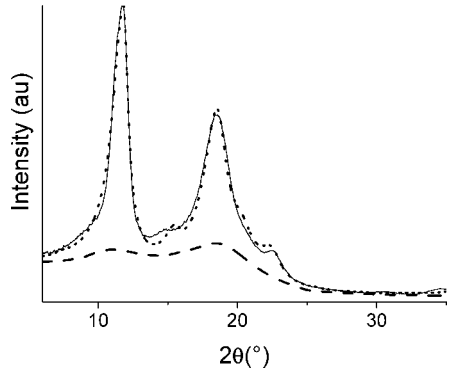


Figure 7. Experimental (continuous line) diffraction patterns of diheterotactic polynorbornene. The calculated profile (dotted line) for the *C*2/*c* model with 9.66Å chain periodicity and the baseline (dashed line) used as background are also shown.

Lowering the symmetry to $p\bar{1}$ might however lead to an altered scenario: crystalline polymorphs with the more contracted chain conformation appear at present to be less probable but cannot be ruled out. Given the intrinsic limitations of the available force fields[17] and the quality of experimental diffraction patterns, the issues involved are very delicate and need further, more detailed investigations which are in progress.

Concluding Remarks. Polymerization of norbornene with the $CrCl_2$(dppa)−MAO catalyst allowed us to synthesize a new stereoregular 2,3-*exo*-diheterotactic polymer characterized by regular sequences of (*mr*) triads. It represents the first example of this stereochemistry obtained by means of stereospecific polymerization of olefins. As also shown in a recent work by Fink,[3] our investigation indicates that unsuspected stereochemistries may result polymerizing a bulky, strained olefin as norbornene with stereospecific catalysts. Work is in progress to devise a polymerization mechanism which may explain the formation of a diheterotactic polymer; a 2-fold control on the stereochemistry of the growing polymer chain must result from the catalyst structure with the coordinated ligands and from the stereochemistry of the last two previously inserted monomer units (chain control). We are also examining the polymerization of norbornene with catalysts based on different Cr(II) bidentate phosphine complexes in order to clarify the role of the catalyst structure (i.e., the type of phosphine ligand bonded to the chromium atom) on the polymerization stereospecificity.

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Supporting Information Available: Tables of refined nonstructural parameters and fractional coordinates for 2,3-*exo*-diheterotactic polynorbornene and text discussing how the data were obtained. This material is available free of charge via the Internet at http://pubs.acs.org.

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