Electronic Supplementary Information (ESI)

Synthesis, chain conformation and crystal structure of poly(norbornadiene) having repeating 3,5-enchained nortricyclene units.

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Experimental

Materials.

Heptane (Merck, 99%) was dried by refluxing for 10h over K-diphenylketyl and then distilled and stored over molecular sieves under nitrogen. Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD, Merck 98%) was dried over CaH_2 at 60 °C under nitrogen for 4h and distilled under reduced pressure. Et_2AlCl (Merck, 97%), $TiCl_4$ (Merck, 99.9%), toluene (Merck, 99.8%) and deuterated solvent for NMR measurements ($C_2D_2Cl_4$, Merck, >99.5/ atom D) were used as received without further purification.

General polymerization procedure.

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. Polymerizations were carried out in a 25 mL Schlenk flask. The reactor was first heated to 110 °C under vacuum for 1h and backfilled with nitrogen. The reactor was then charged with heptane, the appropriate amount of NBD (4.3 mmol when NBD/Ti = 5, and 13.0 mmol when NBD/Ti = 15) and then brought to the polymerization temperature of 0 °C. The

polymerization was started by adding Et_2AlCl (1.73 mmol, 0.21 mL) and $TiCl_4$ (0.867 mmol, 0.09 mL), and stopped with methanol containing a small amount of hydrochloridric acid. The precipitated polymers were collected by filtration, repeatedly washed with fresh methanol and finally dried in vacuum to constant weight. In the case of sample PNBD15, the high amount of material collected allowed to fractionate it by extraction with boiling solvents with a Kumagawa extractor. The fractionation gave a fraction soluble in heptane (2% of the total), a fraction soluble in boiling toluene (20% of the total) and an insoluble residue (78% of the total).

Characterization.

FTIR spectra were acquired using a Perkin-Elmer Spectrum Two in attenuated total reflectance (ATR) mode in the spectral range of 4000–500 cm^{-1} (Figure S1). NMR spectra were recorded on a Bruker NMR advance 400 Spectrometer equipped with a SEX 10 mm probe with automatic matching and tuning, operating at 400 MHz (^{1}H) and 100.58 MHz (^{13}C) working in the PFT mode at 103 °C. Experiments were performed dissolving about 65 mg of the polymer in $C_2D_2Cl_4$ in a 10 mm tube and referred to HMDS as internal standard. The molecular weight average (M_n), and molecular weight distribution (M_w/M_n) were obtained by a high temperature Waters GPCV2000 size exclusion chromatography (SEC) system using an online refractometer detector. The experimental conditions consisted of three PL Gel Olexis columns, ortho-dichlorobenzene (DCB) as the mobile phase, 0.8 mL/min flow rate, and 145 °C. The calibration of the SEC system was constructed using eighteen narrow M_w/M_n PS standards with M_w ranging from 162 to 5.6×10^6 g/mol. For SEC analysis, about 12 mg of polymer was dissolved in 5 mL of DCB.

X-ray powder diffraction patterns were obtained with Ni-filtered CuKα radiation (λ = 1.5418 Å) with an Empyrean diffractometer by PANalytical operating in θ/θ reflection geometry. The degrees

of crystallinity (x_c) were evaluated from the X-ray powder diffraction profiles by the ratio between the crystalline diffraction area and the total area of the diffraction profile.

Thermogravimetric analysis (TGA) was performed using a thermogravimetric analyzer (TGA4000) by Perkin Elmer, by heating the sample from 30 to 900 °C at 10 °C/min in a flowing N_2 atmosphere. DSC measurements were performed using a differential scanning calorimeter DSC Mettler 822 in a flowing N_2 atmosphere at rate of 10 or 40 °C/min.
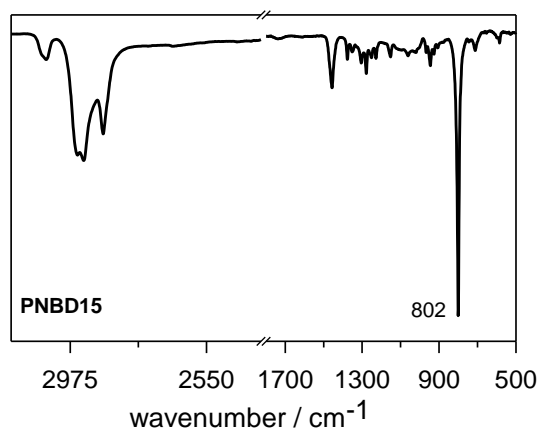

Figure S1. FTIR spectra of the sample PNBD15 obtained from the polymerization of NBD at NBD/Ti = 15 (Table 1 in the manuscript).


Conformational analysis and packing

Conformational and packing energy calculations were performed with the CERIUS^2 software package using the force field COMPASS in the CERIUS program.

Minimum energy conformation of nortricyclene units substituted in the 3,5 positions in the **xx** and **xn** configurations (Scheme 3) were built up starting from the minimum energy of the cyclopentane ring designed by the C atoms 2-6 of the Scheme 3 (see Scheme S1), through the progressive addition of relevant covalent bonds and lateral substituents.

It is well-known that cyclopentane exhibits a nonplanar (puckered) conformation with dihedral angles largely deviating from zero. The potential energy surface of cyclopentane is flat, and the

ring freely pseudorotates between twist and envelope isoenergetic conformations having alternatively C_2 and C_s symmetry, respectively (Scheme S1)[S1-S6]
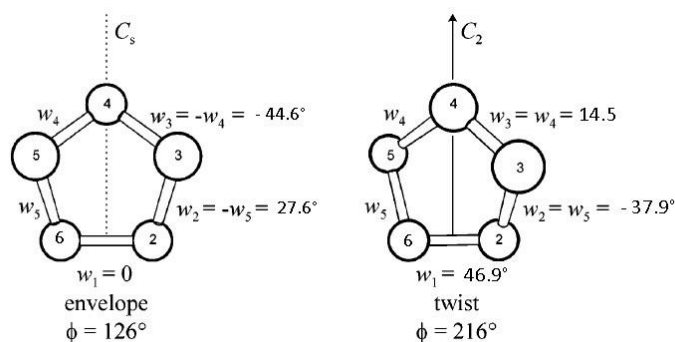
Scheme S1. Puckered conformation of cyclopentane. The values of the torsion angles (w_k) corresponding to a phase angle of puckering (Φ) equal to 126° (envelope form having C_s symmetry) and 216° (twist form having C2 simmetry) are indicated (*vide infra*).

To describe the pseudorotation phenomenon, the following expression for the torsion angles, w_k, was proposed:[S2-S7]

$$w_k = w_0 \cos(4\,\pi Ck/5 + \Phi) \qquad k = 1, 2, 3, 4, 5 \qquad \text{(Eq. S1)}$$

where w_0 is the puckering amplitude, C the conversion factor from radians to degrees, and Φ the phase angle of puckering. Conformations described by Φ values equal to 0°, 36°, 72°, ... correspond to twist forms with C_2 symmetry; those described by Φ values of 18°, 54°, 90°, ... correspond to envelope forms with C_s symmetry. As Φ varies from 0° to 360°, the structure goes through all possible C_2 and C_s forms.

In our calculations, the energy minima correspond to values of w_0 equal to 46.9° in Eq. S1 (see Scheme S1). These results compare well with those reported in the literature.[S1,S4,S8,S9,S10]

The values of the torsion angles (w_k) corresponding to a phase angle of puckering (Φ) equal to 126° (envelope form having C_s symmetry) and 216° (twist form having C_2 symmetry) are indicated in the Scheme S1.

Model structures of 3,5-dimethyl tricyclo[2.2.1.0^{2,6}]heptane units were built up starting from all possible envelope and twist conformers of the five membered ring defined by C2, C3, C4, C5 and

4

C6 carbon atoms of the Scheme 3, found for cyclopentane, by adding the bridgehead atoms 1 and 7 bridging atoms 2-6 and 1-4, respectively, forcing atoms 2 and 6 to form a covalent bond, and finally placing methyl substituents at 3,5 positions in the exo-exo and exo-endo orientations. Regardless of initial starting point, minimum energy conformations for the **xx** and **xn** 3,5-dimethyl tricyclo[$2.2.1.0^{2,6}$] heptane converged toward the model structures of Figure 4. The values of torsion angles θ_1 and θ_2, external to the ring, and of the dihedral angles internal to the five-membered ring formed by atoms C2, C3, C4, C5 and C6 (w_k, Scheme 3), corresponding to the minimum of the conformational energy of **xx** and **xn** units of 3,5-dimethyl tricyclo[$2.2.1.0^{2,6}$]heptane, are reported in Table 3. As discussed in the main text, the cyclopentane rings (formed by atoms C2, C3, C4, C5 and C6 of Figure 4A) adopt minimum energy conformation having a perfect C_s symmetry ($w_1 = 0$, $w_2 = - w_5$, $w_3 = - w_4$) in the case of **xx** configurational isomer (Table 3), a slight distorted C_s symmetry in the case of **xn** configurational isomer.

After modeling the **xx** and **xn** 3,5-dimethyl tricyclo[$2.2.1.0^{2,6}$]heptane base units of Figure 4, the analysis was extended to model dimers in diisotactic and disyndiotactic configurations resulting from enchainment of couples of **xx** units (**xx-xx** model dimer) and **xn** units (**xn-xn** model dimer) (Scheme 4). In the latter case the head-to tail (**xn-xn**), head to head (**xn-nx**) and the tail to tail (**nx-xn**) enchainments were also considered (Scheme 4).

Mixed dimers consisting in monomer sequences of the kind **xx-xn** or **xx-nx** were also considered (Scheme S2).
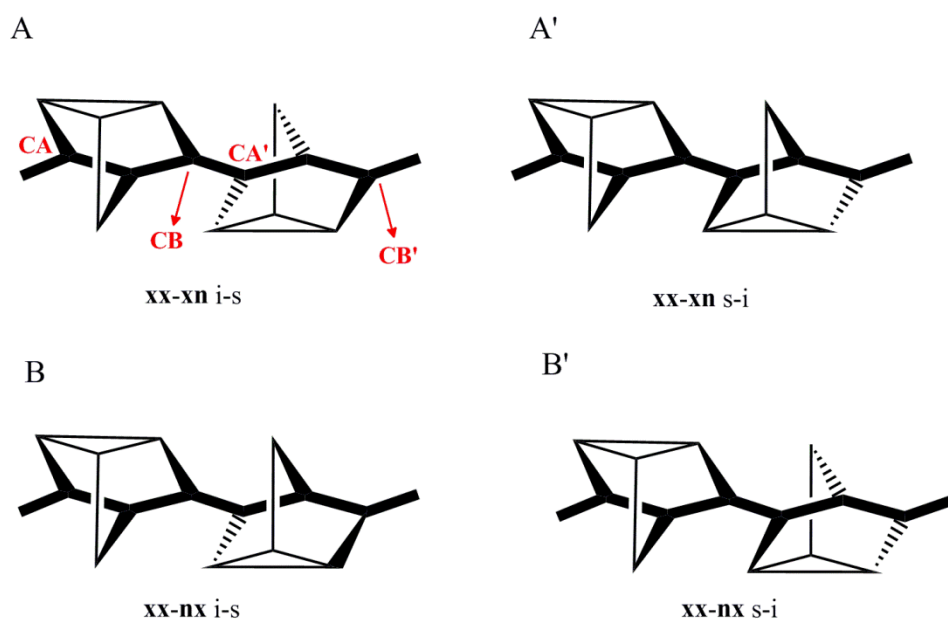
Scheme S2. Dimeric units obtained by connecting the exo/exo (**xx**), exo/endo (**xn**) and endo/exo (**nx**) monomeric units. The symbol i and s indicate isotactic and syndiotactic, respectively, relative arrangements of the couples of carbon atoms CA, CA' and CB, CB'.

The conformational energy profiles calculated as a function of the dihedral angles θ3 (Scheme 5) relative to the ditactic dimeric models of the Scheme S2 are reported in Figure S2. The models of conformations of the dimers of PNBD corresponding to the conformational energy minima of Figure S2 are shown in the Figure S3.
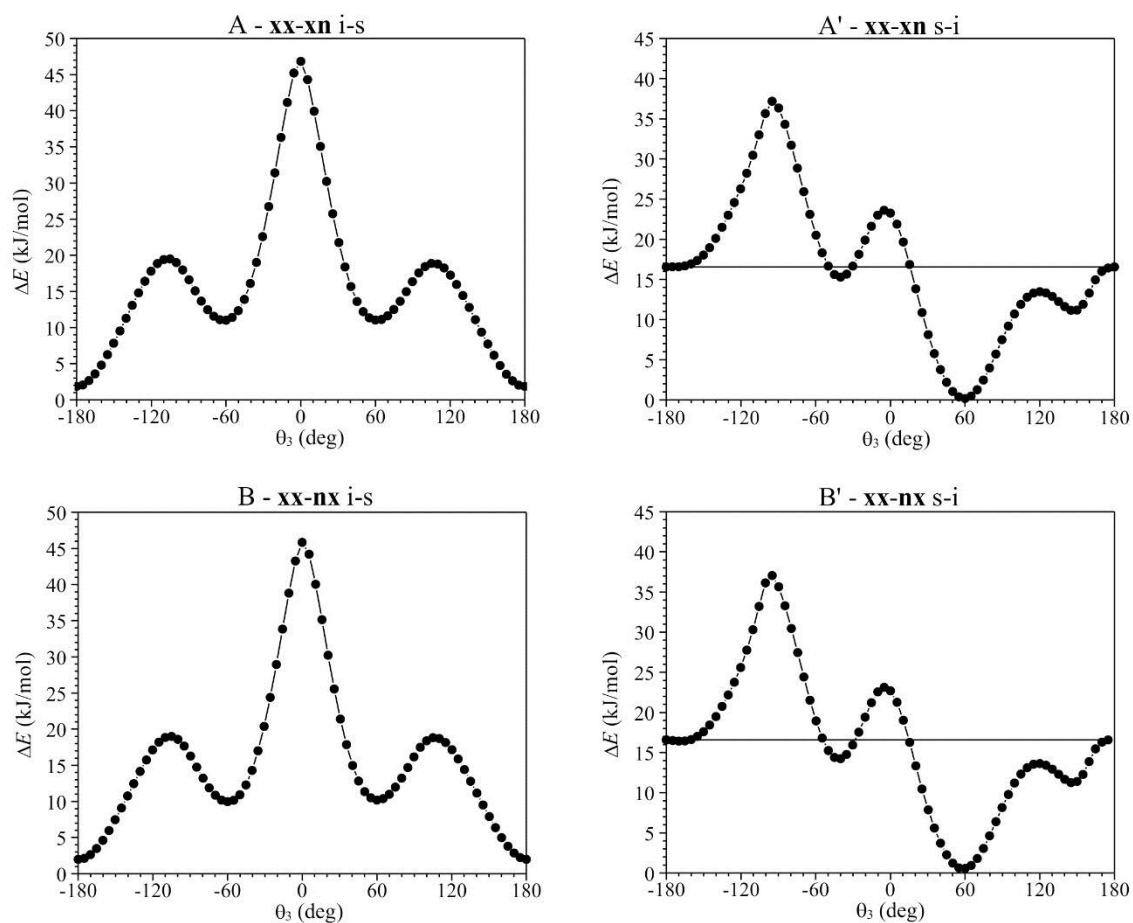
Figure S2. Conformational energy ΔE (= $E − E_{min}$) calculated as a function of the dihedral angles θ_3 (Scheme 5) for the isotactic-syndiotactic model dimers of the Scheme S2. The values of energy are subtracted for the absolute minimum E_{min} relative to the **xx-xn s-i** model dimer.

A - xx-xn i-s   **A' - xx-xn** s-i

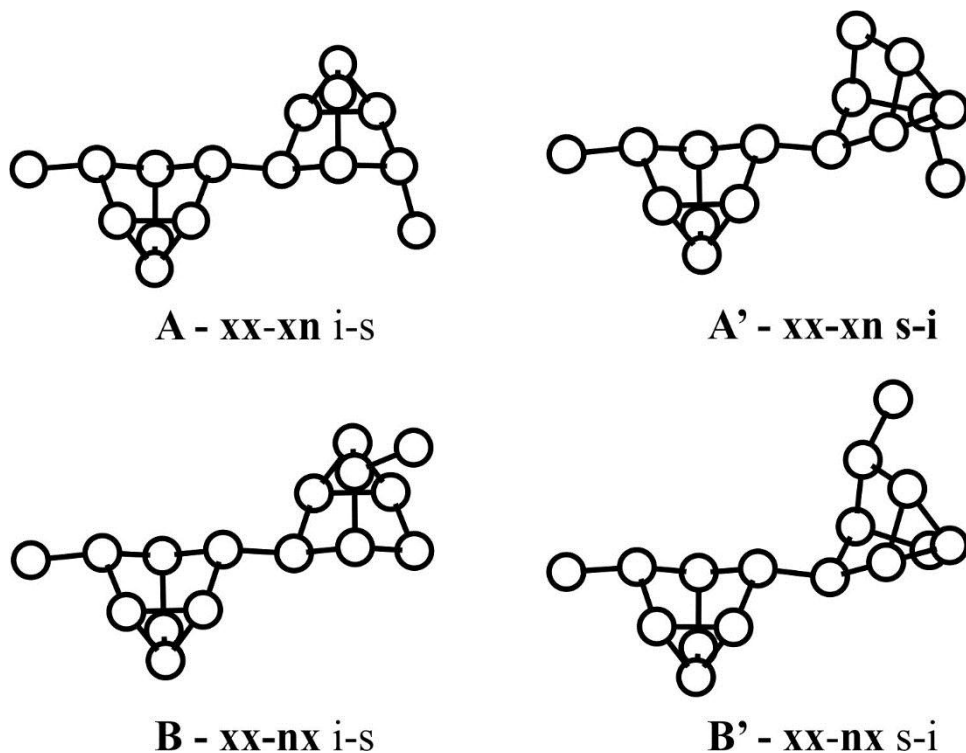**B - xx-nx** i-s   **B' - xx-nx** s-i

Figure S3. Models of the conformation for the dimeric species of the Scheme S2 corresponding to the conformational energy minima of Figure S2.

The fractional coordinates of the models of packing of Figures 8A and B are reported in Tables S1 and S2, respectively, whereas the fractional coordinates of the model of Figure 8C that gives the best agreement between calculated and experimental X-ay powder diffraction profiles are reported in the main text in the Table 6. The atoms of the asymmetric units labelled in the Tables 6, S2 and S3 corresponds to the atoms reported in the Figure S4.
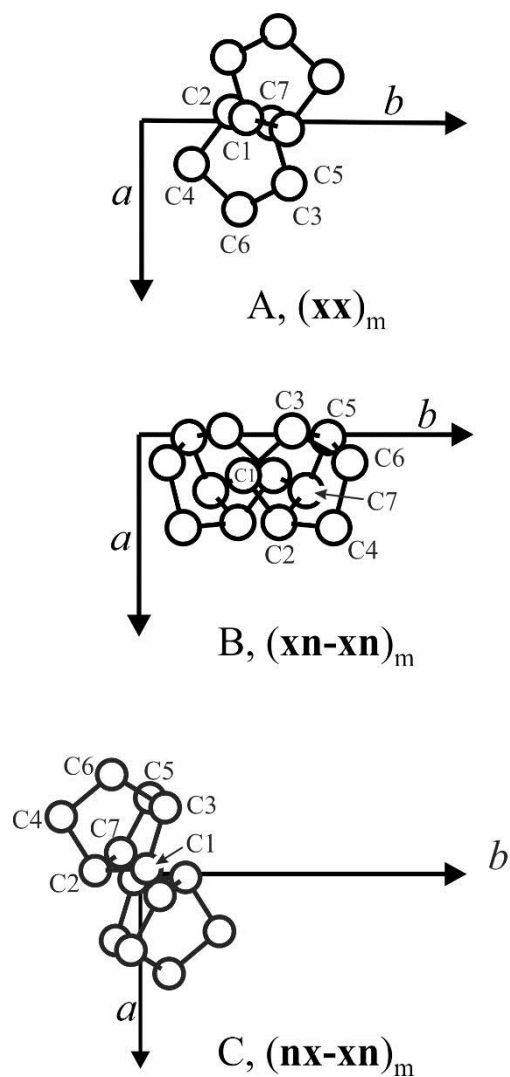
Figure S4. Atoms of the asymmetric units with corresponding labels reported in Tables 6, S2 and S3 in the models of packing of Figure 8A (A), B (B) and C (C) of PNBD in the orthorhombic unit cell with axes a = 6.6 Å, b = 11.0 Å, c = 7.58 Å and space $P2_1/b$ (A), c = 6.42 Å and space group $P2_1/c$ (B) and c = 6.84 Å and space group $P2_1/c$ (C).

Table S1. Fractional coordinates of the atoms of the asymmetric unit in the model of packing of Figure 8A of isotactic chains (**xx**)$_m$ of PNBD with **s**(2/1) symmetry in the orthorhombic unit cell with axes a = 6.6 Å, b = 11.0 Å and c = 7.58 Å and space group $P2_1/b$. The labels H (Cn) indicate the hydrogen atoms linked to the carbon atom Cn (Figure S4A).

Atom	x	y	z
C1	0.009	0.277	-0.343
C2	-0.031	0.191	-0.500
C3	0.225	0.315	-0.400
C4	0.156	0.107	-0.500
C5	0.225	0.315	-0.600
C6	0.316	0.209	-0.500
C7	0.009	0.277	-0.500
H(C1)	-0.095	0.355	-0.352
H(C2)	-0.179	0.145	-0.500
H(C3)	0.312	0.378	-0.320
H(C4)	0.164	0.047	-0.384
H(C4)	0.164	0.047	-0.616
H(C5)	0.312	0.378	-0.680
H(C6)	0.478	0.187	-0.500
H(C7)	-0.095	0.355	-0.648

Table S2. Fractional coordinates of the atoms of the asymmetric unit in the model of packing of Figure 8B of syndiotactic chains (**xn-xn**)$_m$ of PNBD with **t**c symmetry in the orthorhombic unit cell with axes a = 6.6 Å, b = 11.0 Å and c = 6.42 Å and space group $P2_1/c$. The labels H (Cn) indicate the hydrogen atoms linked to the carbon atom Cn (Figure S4B).

Atom	x	y	z
C1	0.143	0.218	-0.172
C2	0.307	0.293	-0.286
C3	-0.013	0.320	-0.153
C4	0.325	0.407	-0.153
C5	0.010	0.396	-0.348
C6	0.098	0.441	-0.145
C7	0.196	0.350	-0.473
H(C1)	0.083	0.147	-0.276
H(C2)	0.453	0.248	-0.315
H(C3)	-0.160	0.302	-0.082
H(C4)	0.392	0.390	0.000
H(C4)	0.421	0.476	-0.228
H(C5)	-0.124	0.430	-0.425
H(C6)	0.052	0.522	-0.062
H(C7)	0.285	0.429	-0.526

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