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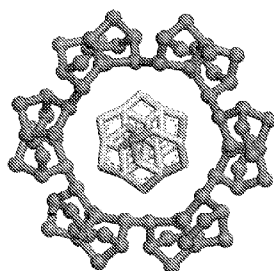
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FIG. 5: 2,3-*exo*-disyndiotactic PNB chain model with intramolecular channel occupied by disordered benzene molecules.



(57) Abstract: It is described the production of crystalline 2,3 disyndiotactic polynorbornene with a decomposition (without melting) temperature in the range 380-400 °C characterized by insolubility in aromatic hydrocarbons at room temperature and partially soluble in boiling toluene. The production process, the crystal structure and new clathrate structures of PNB formed by polymeric helices with tubular internal cavities are also described.



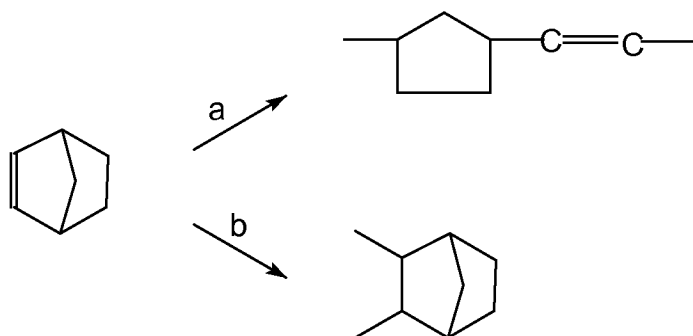
**NORBORNENE POLYMERS AND COPOLYMERS WITH A STEREOREGULAR 2,3
DISYNDIOTACTIC STRUCTURE: THEIR PREPARATION PROCESSES AND
CLATHRATE STRUCTURES INVOLVING THE SAME**

DESCRIPTION

The object of the present invention are new 2,3 disyndiotactic stereoregular crystalline polymers and copolymers of norbornene, their preparation processes and clathrate structures involving the mentioned macromolecules.

It is known that norbornene (NB) may be polymerized along three different routes:

- a) by ring-opening metathesis polymerization (ROMP), affording high molecular weight polymers containing unsaturated monomers; Scheme 1, **a**)
- b) by vinyl addition polymerization affording high polymers containing saturated monomer units
- c) by using cationic initiators, which yield low molecular weight products displaying non-regular structure.

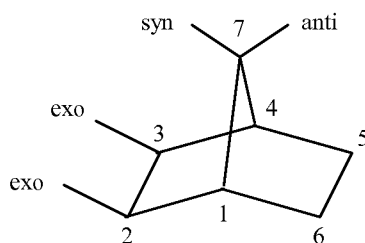


Scheme 1

Polymers obtained according to route **a** have been investigated since long ago and have found various industrial applications, especially as elastomers. Polymers obtained via the cationic route have low practical interest. The present invention relates to polymers of the kind obtained by route **b**, which are usually called “vinyl-type polynorbornenes”.

Various transition metal based catalysts have been used to obtain such polymers. Those involving Ni compounds are among the most used. The polymers which are obtained contain saturated units (see scheme 1, **b**) but are shown to be amorphous by X-ray diffraction analysis. The absence of crystallinity results from the absence of steric order in the macromolecules. Every monomer unit in a polymer formed according to Scheme 1**b** presents

two asymmetric carbons in the main chain. If reaction at the double bond occurs with *cis* opening, as in all polymerizations with transition metal based catalysts, the two asymmetric carbon atoms of each chemical repeat unit (carbon 2 and carbon 3 in the scheme below) present opposite configuration, one presenting S configuration while the other is R. A polynorbornene consisting of this kind of units can only crystallize if there is order in the sequence of configurations of the asymmetric carbon atoms of each chain.



Scheme 2

The two simplest types of stereoregularity which a vinyl-type polynorbornene may display are the following two:

A Di-isotactic polymer: R-S—R-S—R-S—R-S—R-S—

B Disyndiotactic polymer: R-S—S-R—R-S—S-R—R-S— (see Figure 1)

Lido Porri, one of the present inventors, has published¹ with collaborators, the isolation of norbornene oligomers, and specifically a heptamer, using a catalytic system made of aluminium diethylchloride and titanium tetrachloride, with a norbornene/TiCl₄ molar ratio less than 14. Oligomers were obtained, with an amorphous fraction of about 85% in mass soluble in diethyl ether, while the remaining crystalline fraction consisted of a NB heptamer with a melting point of 267°C and a 2,3-*exo*-disyndiotactic structure.

G. Sartori and collaborators published² in 1963 obtaining norbornene polymers polymerizing at 0 °C, using a catalytic system which consisted of aluminium triisobutyl and titanium tetrachloride in a molar ratio Al/Ti = 0.5. The polymer was crystalline, melting at about 115 °C and was soluble at room temperature in aromatic hydrocarbons.

None of the vinyl-type poly(NB) known to date, shows however stereoregularity features that, in association with a high degree of polymerization, are able to confer structural and physical properties which make the material of high application potential.

W.Kaminsky et al³, Makromol Chem., Macromol. Symp., 47, 83 (1991), described a NB polymer obtained with a Zr indenyl catalyst with a diisotactic structure, completely insoluble, with melting point in vacuum higher than 600°C and decomposition at about the same temperature. Subsequent work by Fink and collaborators⁴ (*Angew. Chem. Int. Ed.* **43**,

2444 (2004) on the polymers obtained with closely related Zirconocene catalytic systems indicates structures in which 2,3-diisotactic stereochemistry alternate with connectivities at C7 (numbering as in Scheme 2).

The polynorbornenes obtained with β -diketonate-Ti/MAO catalysts described by Mi X. et al⁵ contain varying amounts of units resulting from ROMP reaction (Scheme 1 a) and units resulting by vinyl addition polymerization units (Scheme 1 b). They are thus non-regular and amorphous (as apparent from the X-ray diffraction patterns) and present no indication of stereoregularity.

A crystalline disyndiotactic norbornene polymer was completely unknown and has now been surprisingly obtained with a decomposition point without fusion higher than 300 °C, preferably higher than 350 °C, and more preferably between 380 and 400 °C. This polymer is insoluble at room temperature in aromatic hydrocarbons while it is partly soluble in boiling toluene.

An other aspect of the invention relates to a preparation process of crystalline 2,3-exo-disyndiotactic polynorbornene by NB polymerization with catalytic systems comprising a transition metal belonging to Groups 4-10 of the Periodic Table of the Elements (new notation) and aluminium alkyls or alumoxanes. The transition metal compound is preferably a Ti halide, and more preferably TiCl_4 or TiCl_3 .

The polymer may be obtained, as indicated above, with the transition metal compound in combination with various aluminium alkyls of general formula AlRX_2 , AlR_2X or $\text{Al}_2\text{R}_3\text{X}_3$, where R is an alkyl or aryl group and X is a halogen, preferably Cl. The Al/Ti ratio may be varied over a broad range (from 0.5 to 40), but preferably it is kept between 1 and 20, and more preferably between about 2 and 10.

The catalyst may be prepared by reacting first the aluminium alkyl compound with TiCl_4 and subsequently adding the monomer (preformed catalyst), or else adding the aluminium compound to the mixture of TiCl_4 and the polymerization solvent (catalyst prepared in situ). With the preformed catalyst, the ratio monomer/ TiCl_4 may be varied over a broad range, but it is preferably kept above 14 to minimize formation of low molecular weight polymers. With the in situ prepared catalyst it is necessary to operate above a ratio of about 14 to obtain the crystalline polymer.

The polymerization may be carried out in a broad temperature range, from about -80 to +80°C, but preferably between 0°C and ambient temperature, and specifically between 0 and 30°C. The operative modes are detailed in the enclosed examples.

The structure of the obtained crystalline polynorbornene was determined on the basis of X-ray diffraction spectra combined with molecular modelling methods.

The poly(NB) obtained with the above catalysts is of the vinyl-type, and consists therefore of **b** type units (Scheme 1) and presents a disyndiotactic structure. A poly(NB) with this structure was up to now unknown.

The polymerization product consists of an ether soluble fraction, which is amorphous upon X-ray examination, and of an ether-insoluble fraction showing high crystallinity. The ratio between the amorphous fraction and the crystalline fraction mainly depends on the polymerization time; in polymerizations of 80-90 hours at room temperature the ether-soluble fraction reduces to less than 10% (Table 1).

The crystalline fraction is partly soluble in boiling toluene. The molecular weight of the toluene soluble fraction has been determined by GPC. Most of the product has a molecular weight around 4000. The molecular weight of the insoluble fraction has not been determined, because of its insolubility.

Thermal analysis of the toluene soluble fraction and of the residual to the toluene extraction does not present observable thermal transitions up to 380°-400°C, at which temperatures degradation phenomena start to become relevant.

The crystalline polymers are characterized by a ^{13}C NMR spectrum (Figure 2) presenting an intense resonance at 35.44 ppm, typical of C7 in disyndiotactic sequences. Low intensity resonances at 33.3 e 34.3 ppm, also present in other known PNB, are likely due to C7 in terminal units or non-stereoregular sequences.

The X-ray diffraction patterns of the crystalline fraction soluble in boiling toluene and of the insoluble residual are identical. Strong evidences exist that X-ray diffraction patterns of disyndiotactic PNB are in essence invariant, except for the width of the diffraction maxima, from degrees of polymerization (DP) 15 upwards.

The crystalline and molecular structure of the polymer has been determined by a Rietveld approach on the basis of powder X-ray diffraction patterns, combining molecular modelling methods and using also indications and geometrical data, from a recent single crystal investigation of the structure of a heptamer obtained with a catalyst of the same family as the one used to obtain the polymer which is the object of the present patent. With the mentioned methodology it was possible to assign unequivocally the 2,3-exo-disyndiotactic stereochemistry to the synthesized crystalline PNB. X-ray diffraction patterns (Cu-K α) were recorded in reflection mode using an Italstructure θ/θ diffractometer and in transmission with a Bruker P4 diffractometer equipped with a two-dimensional Hi-Star detector. In the latter

case, samples mounted on a glass fibre were used, with a sample to detector distance of about 10 cm. In the modelling study, carried out to determine the atomistic details of the structure of the 2,3-exo-disyndiotactic polymer, molecular mechanics approaches were used which were validated with semiempirical studies of related model systems. In particular, several models have been studied using different force fields as the COMPASS⁶ force field in the Material Studio package⁷ which allowed the analysis of both isolated and packed chain structures with and without symmetry constraints. This force field was recently successfully adopted in the analysis of the structure of a diheterotactic polynorbornene with main chain sequences⁸.

Figure 1 reports a schematic representation of the fully extended macromolecule with an -R-S-S-R-R-S- sequence of asymmetric carbon atoms along the main chain. To investigate the isolated PNB chain, several models were set up considering diisotactic and disyndiotactic stereochemistry with different numbers of monomers in the asymmetric unit. The majority of the models displayed very high conformational energy. Acceptable energies were found only for disyndiotactic chains with 6₁ screw axis symmetry with a chain repeat of about 10 Å. In this conformation, the repeating unit consists of two norbornene rings with a sequence of torsion angles $|\theta_1| |\theta_0| |\theta_2| |\theta_0|$ with the following approximate values $|169^\circ| |2^\circ| |-127^\circ| |2^\circ|$ (Figure 1). The relaxation of symmetry constraints did not alter the backbone conformation and the energy of the isolated chain. This result was confirmed by quantum mechanics calculations on chain models which were then used to model the crystalline phase of the polymer fitting the X-ray diffraction data. The 6₁ helical symmetry of the chains is compatible with a hexagonal packing of the macromolecules and using *P*6₁, *P*6₁22 and similar spatial groups favourable conformational and packing energies are obtained together with a very good fit of the calculated powder diffraction patterns with the experimental data. The model obtained for the isolated and packed chain is reported in Figure 3 with lattice parameters of the hexagonal cell $a = b = 14.0 \text{ Å}$, $c = 10.3 \text{ Å}$. The calculated density, 1.088 Mg m^{-3} , compares well with the experimental value of $1.09 \pm 0.05 \text{ Mg m}^{-3}$.

Figure 4 reports: a) the experimental; and b) non-optimized calculated diffraction profiles assuming empty intra-chain cavities. Profile c) is a non optimized profile calculated assuming the presence of benzene molecules into intra-chain cavities.

The calculated diffraction profile in Figure 4b shows reasonable agreement with the experimental (Figure 4a). The numbers of maxima in the experimental diffraction pattern of disyndiotactic polynorbornene ensure the reliability of the structure determination also

considering the high symmetry of the hexagonal lattice and the presence of one single chain in the unit cell.

Table 1 reports the comparison between observed and calculated diffraction maxima for crystalline 2,3-*exo*-disyndiotactic PNB (see the model in Figure 3a) assuming a hexagonal lattice with $a = b = 13.90$ and $c = 10.3$ Å. Reflections $00l$, with $l \neq 6n$ are systematically absent in the $P6_1$ space group.

Table 1.

hkl	$2\theta_o$ (deg)	$2\theta_c$ (deg)	d_o (Å) observed	d_c (Å) calculated	$I/I_{max}(\%)$ observed	$I/I_{max}(\%)$ calculated
100	7.35	7.34	12.02	12.04	vw	65
101	11.23	11.31	7.87	7.82	vvs	100
110	12.69	12.74	6.97	6.95	m	56
200	14.73	14.72	6.01	6.02	m	15
111	-	15.38	-	5.76	-	-
201	16.99	17.06	5.22	5.20	s	19
102	-	18.74	-	4.73	-	-
120/210	19.41	19.51	4.57	4.55	vs	54
121/211	21.17	21.35	4.19	4.16	m	27
112		21.47		4.14		
300	22.38	22.15	3.97	4.01	vw	13
202		22.72		3.91		
301	23.60	23.80	3.77	3.74	vw	4
220	25.95	25.63	3.43	3.48	vw	3
122		26.13		3.41		
130/310	-	26.70	3.34	3.34	-	1
103	-	27.01	3.30	3.30	-	1
221	-	27.08	3.29	3.29	-	1
131	27.97	28.10	3.19	3.18	vw	2
302		28.19		3.17		
113	-	29.01	-	3.08	-	-
400	29.58	29.68	3.02	3.01	vw	0
203		29.96	-	2.98	-	1

A significantly better agreement between calculated and observed pattern, specifically in the low angle portion of the diffraction pattern, can be achieved by taking into account inclusion of various molecular species or chain terminals in the disyndiotactic PNB crystal, as shown in Figure 4c.

In the model proposed for crystalline 2,3-*exo*-disyndiotactic polynorbornene, shown in Figure 3, the conformation adopted by the polymer helices require the formation of tubular cavities or channels at the core of the polymer helices. The 6_1 helix of disyndiotactic polynorbornene is in essence a helical tape, (see Figure 3c) characterized by rather tight van der Waals interactions among successive helical turns. An approximately tubular structure results with accessible internal channels presenting an average diameter of 0.4-0.5 nm and is therefore able to host a broad variety of molecular species. Structures of this kind have never been observed up to now in other materials based on crystalline organic polymers. Up to now known examples exist of systems which crystallize leaving empty intermolecular cavities or channels in the crystalline lattice: the most remarkable case is syndiotactic polystyrene (s-PS)⁹, which, as stated, forms crystal structures where voids occur between different chain stems and not at the core of single helical molecules.

Another aspect of the invention relates to a crystalline disyndiotactic stereoregular norbornene copolymers comprising units derived from substituted norbornene monomers such as 5-Vinyl-2-norbornene 5-Ethylidene-2-norbornene, 5,6-diethyl-norbornene, 5-butyl-2-norbornene, 5-dodecyl-norbornene, 5-phenyl-norbornene), or from unsubstituted or substituted olefin monomers, such as cyclopentene, bicyclo-octene and dicyclopentadiene.

Additional objects of the present invention are inclusion compounds and clathrate structures in which low molecular weight molecules may be trapped inside the described disyndiotactic PNB structure. The ability to form clathrates based on stereoregular disyndiotactic PNB sequences makes these materials highly attractive for separation and chemical recognition applications, as potential vectors of guest species, and in electronic sensing devices. Unique features of disyndiotactic PNB clathration arise due to the fact that the hosting ability is in essence a single-molecule property, and because of the saturated apolar nature of the hosting channels.

Clathrate structures are formed also by using norbornene copolymers as described above. Preferably such structures are characterized for a monomer fraction of at least 10% by moles by helical conformations of stereoregular disyndiotactic sequences of 10-15 monomer units, which form substantially tubular cavities with internal diameters having a size less than 1 nm.

Aside from the model shown in Figures 3 presenting tubular intrachain hollow spaces, a number of models of systems in which the intrachain channels host low molecular mass compounds (like toluene, benzene, heptane, NH_3) were examined both experimentally and with molecular modelling approaches to verify that the intramolecular cavities are selectively and reversibly accessible. These clathrate systems display X-ray diffraction patterns close to the one shown in Figure 4a, provided that the average electron density of the included molecule is not too different from that of PNB itself. This observation is consistent with a disordered organization of the guest within the channels of PNB.

On the contrary well characterized crystalline systems were obtained with I_2 molecules, which have an average electron density substantially higher than PNB, proving unequivocally that the I_2 molecules can be hosted in and released from, the channels of crystalline disyndiotactic PNB (see Figure 6). Both X-ray diffraction evidence and gravimetric methods indicate that up to 2 molecules of I_2 can be hosted and released under vacuum in a unit cell containing also a 12 monomer units disyndiotactic PNB stem.

EXAMPLES

The following examples indicate how the new polymer can be prepared.

Example 1

In a 25 mL glass reactor, supplied with a magnetic stirrer and connected to a vacuum/nitrogen system, are introduced, operating under dry nitrogen:

- 10 mL of anhydrous heptane;
- 0.8 mL of a 1 M heptane solution of TiCl_4 (0.08 mmol of TiCl_4);
- 4.5 mL of a 1.066 M heptane solution of AlEt_2Cl (4.8 mmol of AlEt_2Cl); the solution of AlEt_2Cl is introduced slowly, in the course of 3-4 minutes, under stirring.

The suspension so obtained is kept under stirring for about 10 minutes at room temperature, then g 4.23 (45 mmol) of norbornene are introduced.

The suspension is kept under stirring at room temperature for 24 hours, then the polymerization was terminated by introducing slowly 5 mL of ethanol. The product is then coagulated with an excess of ethanol (ca: 50 mL) acidified with aqueous HCl , repeatedly washed with ethanol, and finally dried in vacuo at room temperature. Yield: 1.22 g of polymer, as a white powder.

Examples 2-11

Operating as for example 1, but using different amounts of reagents under the conditions indicated, the results reported in Table 2 were obtained. All the runs were carried out at 20°C.

Table 2. Polymerization of norbornene with preformed AlEt₂Cl-TiCl₄ catalyst.

Ex.	Catalyst			Polymerization		Polymer			
	Ti Cl ₄ (mmol)	AlEt ₂ Cl (mmol) Al/Ti (mol)	Heptane ml NB mmol	NB/Ti (mol)	Time h	g	Fractionation ^{a)}		
							%	Mn	Mw
1	0.8	4.8 6	16 45	56.25	24	1,22	Ee: 24,5 Te : 38	2476	2758
2	0.4	0.8 2	15 45	112.5	24	0.95	Ee: 45.5 Te : 45.5		
3	0.8	1.6 2	17 45	56.25	24	1.61	Ee: 28.7 Te: 50.5	1839 3076	2409 3652
4	0.8	1.6 2	15 45	56.25	72	3.12	Ee: 9 Te : 34.8		
5	0.8	1.7 2.13	15 45	56.25	72	2.00	Ee: 11.2 Te: 32.8	4445	5891
6	2	12.4 6.2	16 45	22.5	24	2.4	Ee: 27.5 Te: 25.5	1530	1729
7	4	8 2	11 45	11.25	24	3.8	Ee: 51.6 Te: 20.6		
8	4	8 2	8.5 45	11.25	24	3.9	Ee: 25 Te: 60	1020 1800	1230 2100
9	0.8	1.6 2	17 45	56.25	4	0.39	Ee: 77		
10	2	4 2	17 45	22.5	4	0.56	Ee: 50 Te: 23		
11	2	4 2	17 45	22.5	24	3,26 2			

a) Ee: fraction extracted by boiling di-ethyl ether . Te: fraction extracted by boiling toluene. Fractions are expressed by % weight with respect to the total polymerization product.

The catalyst $\text{Al}_2\text{Et}_3\text{Cl}_3$ has been used in Example 11 instead of AlEt_2Cl .

Examples 12-14

A series of preparations have been attempted at 0°C with in situ prepared catalyst. Operating under dry nitrogen, in the reactor we introduced:

- Heptane
- TiCl_4
- Norbornene

AlEt_2Cl is introduced into the mixture under stirring.

The corresponding results are reported in Table 3.

Table 3. Polymerization of norbornene with preformed AlEt_2Cl - TiCl_4 catalyst at 0°C .

Es.	Catalyst			Polymerization		Polymer			
	TiCl_4 (mmol)	AlEt_2Cl (mmol) Al/Ti (mol)	Heptane ml NB mmol	NB/Ti (mol)	Time (h)	g	Fractionation ^{a)}		
							%	Mn	Mw
12	2.0	4.0	12	17.00	28	3,18	Ee: 64,1		
		2	34				Res.16.5	1097	1206
13	2.0	4.0	13	25.0	24	4.69	Ee: 50.		
		2	50				Te: 16.9		
14	0.2	0.4	13	250	27	1.61	Ee: 25.4	1135	1589
							Te: 50.5	4372	6120
		2	50				Res 34.3	4852	6792

Example 15

In a reactor are introduced, operating under dry nitrogen:

Heptane mL 13; TiCl_4 mmol 2; Norbornene mmol 45.

AlMe_2Cl (mmol 4) is then added under stirring. The polymerization is carried out for 24 hours at 0°C . 4.6 g of polymer are obtained, of which:

- 58.8% is soluble in diethyl ether;

- 12.1% is soluble in toluene.

Example 16

Operating as in example 15, but using 0.2 mmol of TiCl_4 and 0.4 mmol of AlMe_2Cl , 1.42 g of polymer are obtained. Fractionation with diethyl ether and toluene gives results similar to those of example 15.

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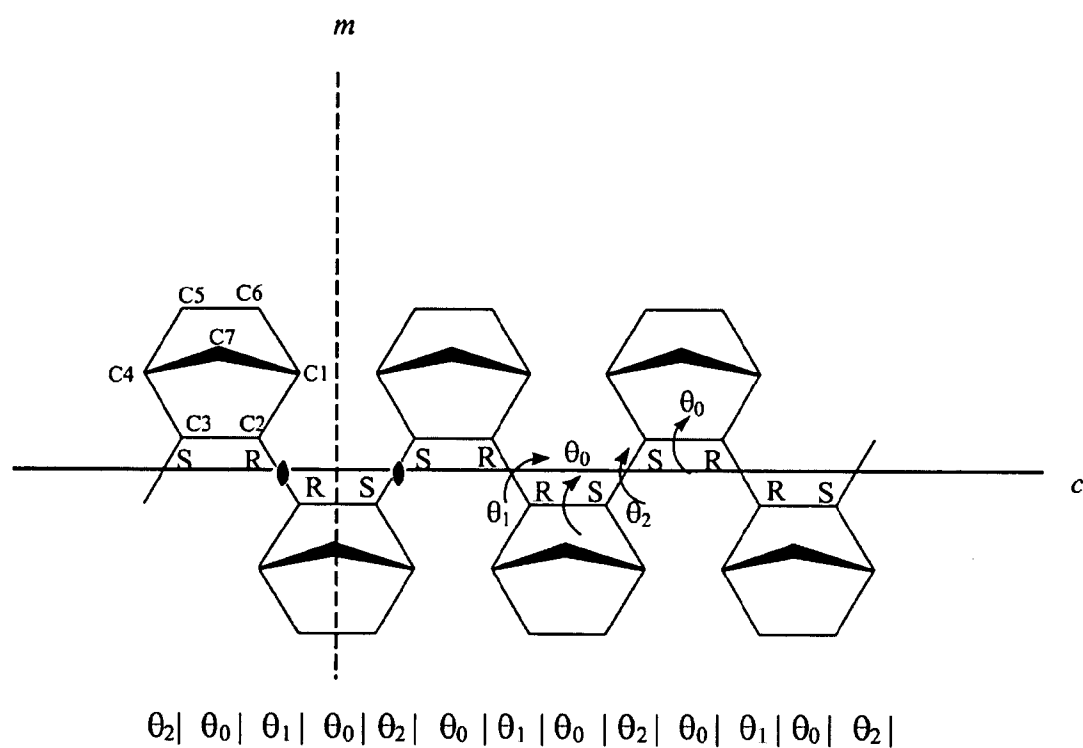
CLAIMS

1. Norbornene polymer with a stereoregular 2,3-disyndiotactic structure having a temperature of decomposition without melting of above 300°C.
2. Norbornene polymer according to claim 1, having a temperature of decomposition without melting between 380 and 400°C.
3. Norbornene polymer according to any of claims 1-2, characterized by being insoluble in aromatic hydrocarbons at room temperature.
4. Norbornene polymer according to any of claims 1-2, characterized by being partially soluble in boiling toluene.
5. Norbornene polymer according to any of claims 1-4, wherein said polymer is a crystalline homopolymer of norbornene characterized by a 2,3-exo-disyndiotactic structure with a 6-fold helical symmetry, or to a symmetry close thereto, and a repeat period of between 8 and 12 Å.
6. Norbornene polymer according to any of claims 1-4, wherein said polymer is a crystalline copolymer of norbornene comprising units derived from substituted norbornene monomers selected from 5-Vinyl-2-norbornene 5-Ethylidene-2-norbornene, 5,6-diethyl-norbornene, 5-butyl-2-norbornene, 5-dodecyl-norbornene, 5-phenyl-norbornene, or from unsubstituted or substituted olefin monomers selected from cyclopentene, bicyclo-octene and dicyclopentadiene.
7. Process for the preparation of 2,3-exo-disyndiotactic polynorbornene, comprising polymerising norbornene in the presence of a catalytic system comprising a compound of a transition metal belonging to Groups 4-10 of the Periodic Table of the Elements (new notation) and an aluminium alkyl or an alumoxane.
8. Process according to claim 7, characterized in that the said transition metal compound is a Ti halogenide.
9. Process according to claim 7, characterized in that the said aluminium alkyl is selected from the group consisting of aluminium alkyls of general formula AlR_nX_{3-n} , wherein R is an alkyl group and X is a halogen.
10. Process according to claim 9, characterized in that the said aluminium alkyl X is Cl.
11. Process according to claim 9, characterized in that the molar ratio Al/Ti is comprised between 0.5 and 40.
12. Process according to claim 9, characterized in that the molar ratio Al/Ti is comprised between 2 and 10.

13. Process according to claim 7, characterized in that the molar ratio NB/Transition metal compound is higher than 14.
14. Process according to claim 7, characterized in that the polymerization temperature is comprised between -80°C and +80°C.
15. Process according to claim 7, characterized in that the polymerization temperature is comprised between 0°C and +80°C.
16. Clathrate structures wherein a polymer, or an oligomer with polymerization degree > 12 of 2,3-exo-disyndiotactic polynorbornene, according to claims 1-6, includes guest molecules.
17. Clathrate structures according to claim 16, wherein said polymer comprises norbornene copolymers with substituted norbornene monomers or with unsubstituted or substituted olefin monomers, wherein said norbornene copolymers are characterized for a monomer fraction of at least 10% by moles by helical conformations of stereoregular disyndiotactic sequences of 10-15 monomer units, which form substantially tubular cavities with internal diameters having a size less than 1 nm.
18. Clathrate structures according to claim 17, wherein said substituted norbornene monomers are selected from 5-Vinyl-2-norbornene 5-Ethylidene-2-norbornene, 5,6-diethyl-norbornene, 5-butyl-2-norbornene, 5-dodecyl-norbornene, 5-phenyl-norbornene.
19. Clathrate structures according to claim 17, wherein said olefin monomer is selected from cyclopentene, bicyclo-octene and dicyclopentadiene
20. Use of clathrate structures according to any of claims 16-18 in processes of molecular recognition, molecular sensing and separation.

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FIG. 1 : Schematic representation of 2,3-*exo*-disyndioctic PNB evidencing the R-S-S-R-R-S- sequence in the main chain.



2/6

FIG. 2 : ^{13}C NMR solution spectrum of del 2,3-*exo*-disyndiotactic PNB

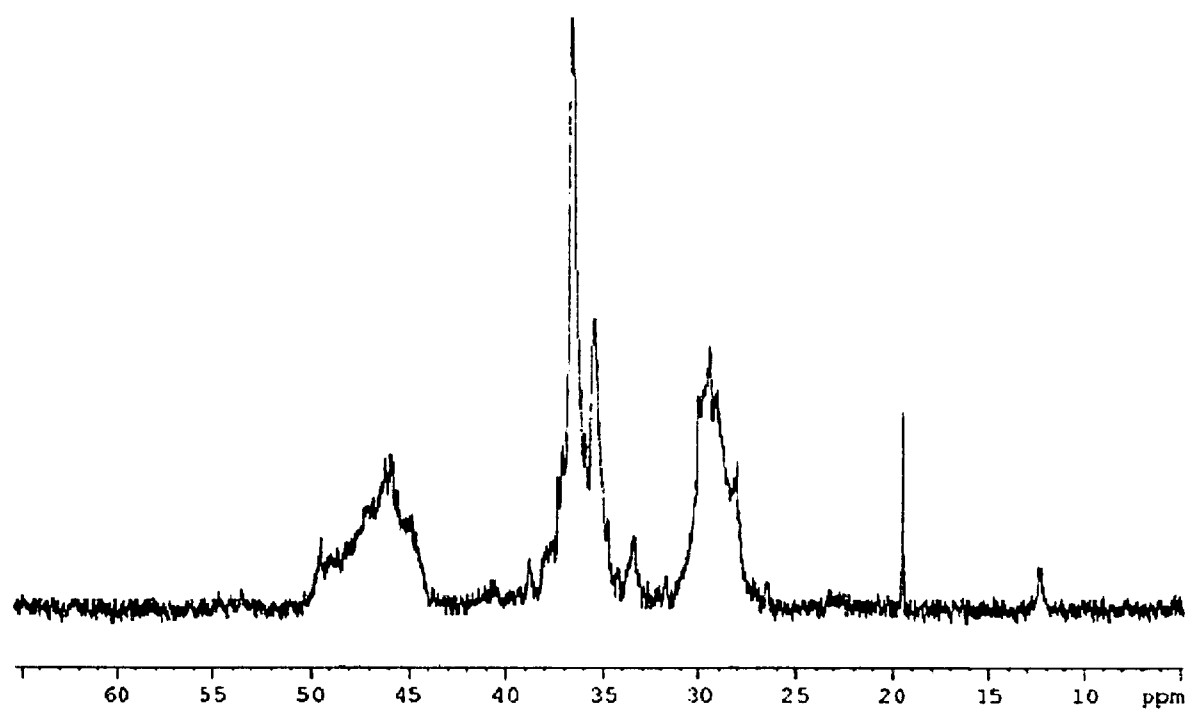


Figure 3a: Crystalline structure of 2,3-*exo*-disyndiotactic PNB (projection down the chain axis)

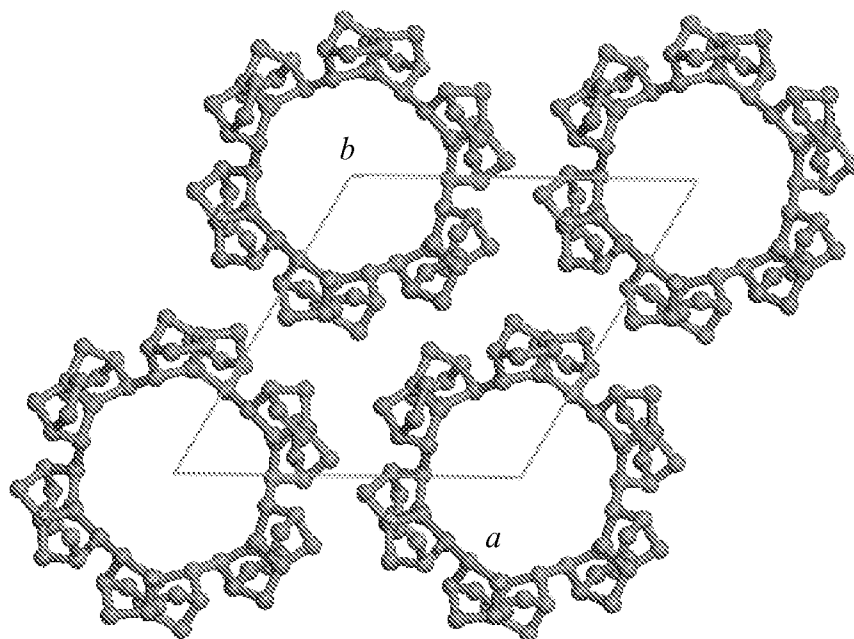


FIG. 3b: Side view of a CPK structural model of the PNB chain

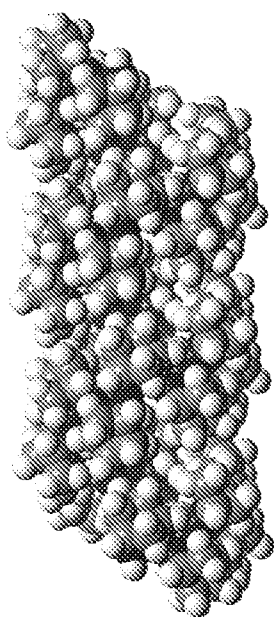


FIG. 3c: Scheme evidencing the helical tape structure of the PNB chain



FIG. 4: Experimental (a), and unrefined calculated X-ray powder diffraction patterns (b e c), for disyndiotactic PNB: (b) is obtained with empty channels and (c) assuming inclusion of two benzene molecules.

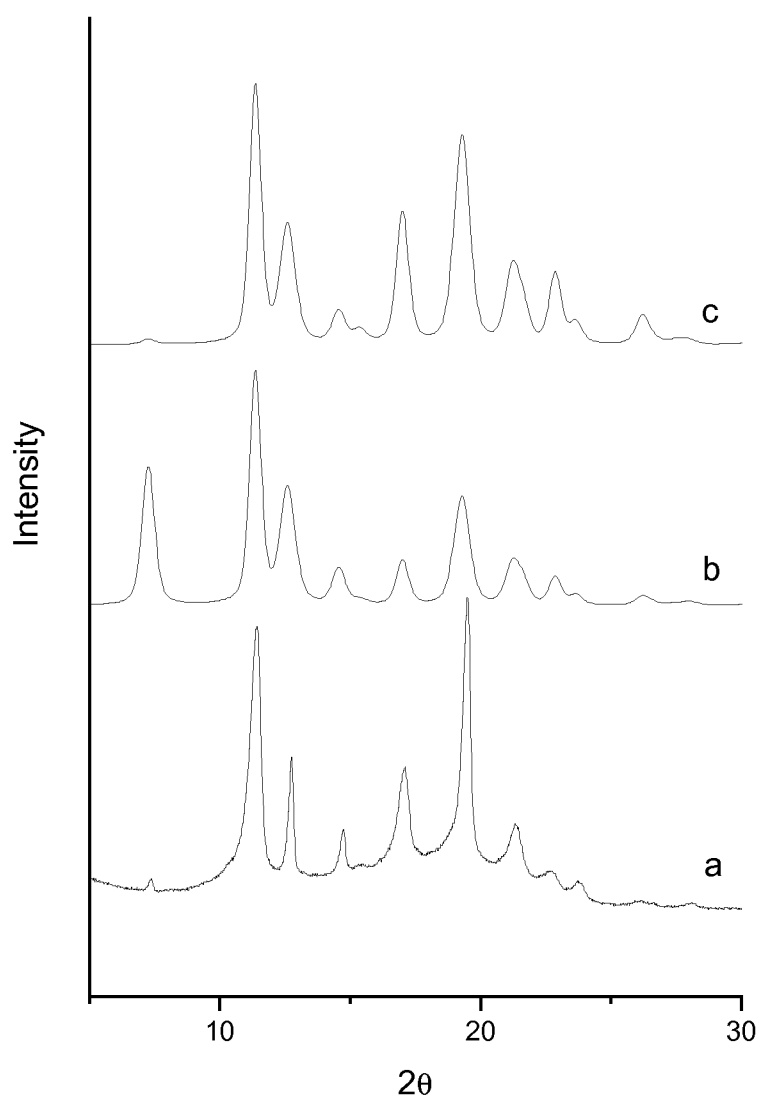


FIG. 5: 2,3-*exo*-disyndiotactic PNB chain model with intramolecular channel occupied by disordered benzene molecules.

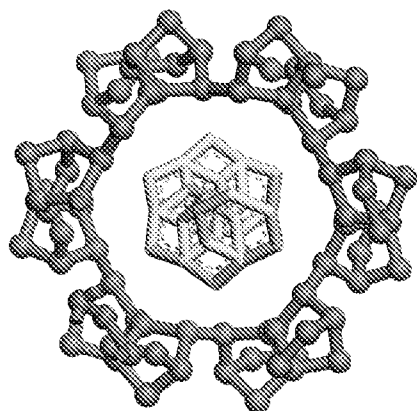


FIG. 6a: diffraction pattern of the crystalline 2,3-*exo*-disyndiotactic PNB/ I₂ adduct.

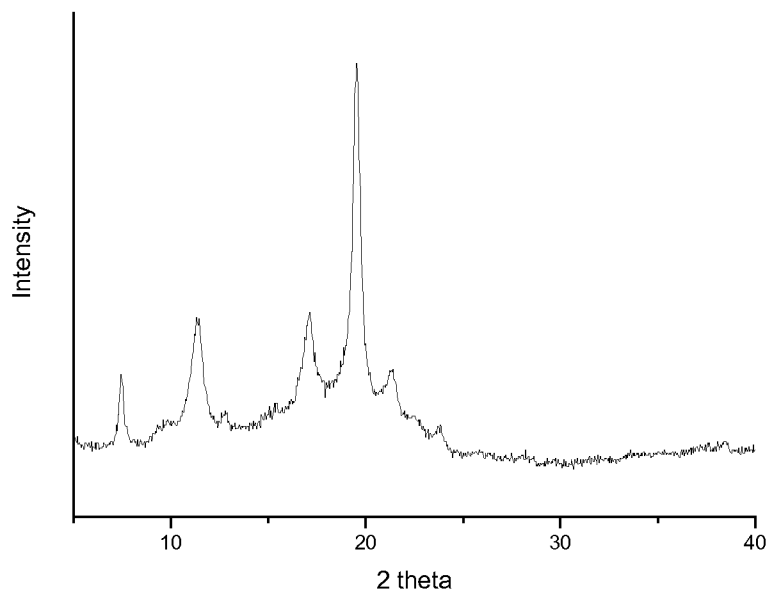
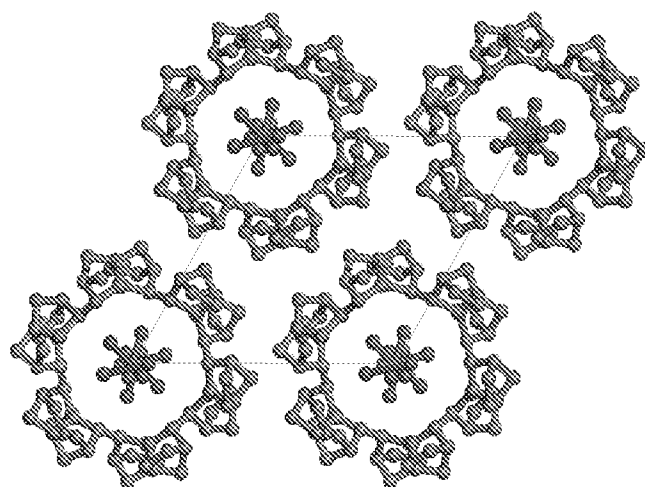


FIG. 6b: 2,3-*exo*-disyndiotactic PNB chain model with intramolecular channel occupied by disordered I₂ molecules.



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/064562

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F32/08 C08F132/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MI X ET AL: "PREPARATION OF POLYNORBORNEN WITH BETA-DIKETONATE TITANIUM/MAO CATALYSTS" POLYMER BULLETIN, SPRINGER, HEIDELBERG, DE, vol. 47, no. 6, 1 February 2002 (2002-02-01), pages 521-527, XP001125824 ISSN: 0170-0839 the whole document ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/064562

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No
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