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TITLE

POLYMERS OF SUBSTITUTED CYCLOPENTENES

FIELD OF THE INVENTION

5 Cyclopentenes which are substituted with various hydrocarbyl groups can be homopolymerized or copolymerized with cyclopentene itself to form polymers useful as molding resins. Nickel and palladium α -diimine complexes can be used as catalysts for these
10 polymerizations, but also disclosed herein are α -diimine complexes which are novel catalysts for the polymerization of cyclopentenes.

TECHNICAL BACKGROUND

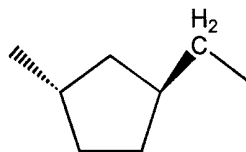
Nickel and palladium α -diimine complexes are known
15 catalysts for the polymerization of various olefins, including cyclopentene itself, see for instance World Patent Application 96/23010. However, methods for polymerization of various substituted cyclopentenes have not been reported with such catalysts.

20 Homopolymers of 3-methylcyclopentene have been reported, see for instance J. Boor, et al., Die Makromolekulare Chemie, vol. 90, p. 26-37 (1966).

World Patent Applications 96/23010 and 98/27124, and U.S. Patent 5,880,241 describe
25 homopolycyclopentenes which are melt processible.

SUMMARY OF THE INVENTION

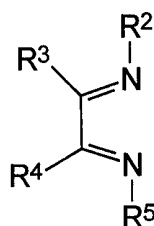
This invention concerns a polymer, comprising, repeat units derived from one or more of
3-methylcyclopentene, 4-methylcyclopentene,
30 3-ethylcyclopentene or 3-cyclopentylcyclopentene, and optionally cyclopentene, provided that when said polymer is a homopolymer of 3-methylcyclopentene, at least about 40 mole percent of repeat units present are of the formula



(II).

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This invention also concerns a process for the polymerization of one or more olefins selected from the group consisting of 3-methylcyclopentene, 4-methylcyclopentene, 3-ethylcyclopentene and 3-cyclopentylcyclopentene, and optionally cyclopentene, by contacting, at a temperature of -100°C to about $+200^{\circ}\text{C}$, said olefin with a olefin polymerization catalyst system containing a nickel or palladium complex of a compound of the formula



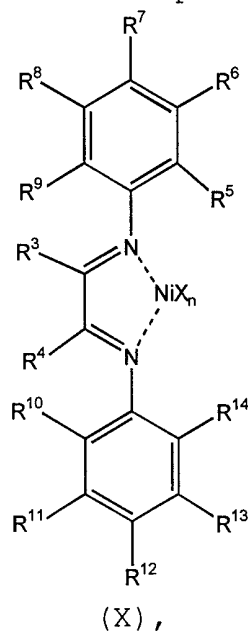
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and optionally other cocatalysts, wherein

R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and

R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring.

Disclosed herein is a compound of the formula

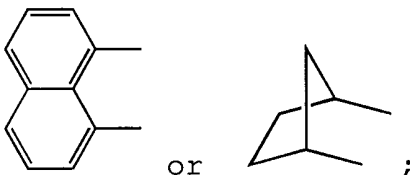


wherein:

each X is independently an anion;

n is 2 or 3;

R³ and R⁴ taken together are



5 R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, and R¹⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

and provided that:

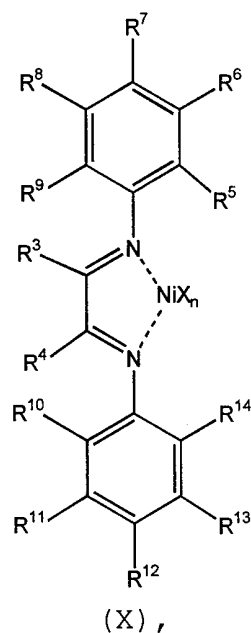
10 when R⁵ is the same as R¹⁰, and R⁹ is the same as R¹⁴, said compound is in an anti form;

no more than one of R⁵, R⁹, R¹⁰, and R¹⁴ is hydrogen;

any two of R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, and R¹⁴ vicinal to one another may form a ring; and

15 R⁵ is different than R⁹.

This invention also concerns a process for the polymerization of one or more of cyclopentene and a substituted cyclopentene, comprising, contacting, at a temperature of -100°C to about +200°C, said olefin with
20 a olefin polymerization catalyst system containing a compound of the formula

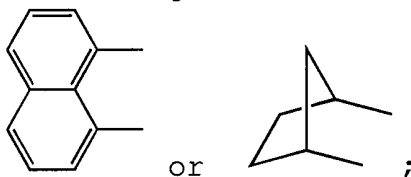


and optionally cocatalysts, wherein:

each X is independently a monoanion;

n is 2 or 3;

R³ and R⁴ taken together are



5 R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, and R¹⁴ are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

and provided that:

10 when R⁵ is the same as R¹⁰, and R⁹ is the same as R¹⁴, said compound is in an anti form;

no more than one of R⁵, R⁹, R¹⁰, and R¹⁴ is hydrogen;

any two of R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, and R¹⁴ vicinal to one another may form a ring; and

15 R⁵ is different than R⁹.

This invention also concerns a homopolycyclopentene that has an end of melting point of 325°C to about 380°C.

DETAILS OF THE INVENTION

20 Herein certain terms are used to define certain chemical groups or compounds. These terms are defined below.

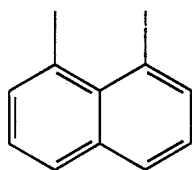
- A "hydrocarbyl group" is a univalent group containing only carbon and hydrogen. If not otherwise stated, it is preferred that hydrocarbyl groups herein contain 1 to about 30 carbon atoms.

- By "substituted hydrocarbyl" herein is meant a hydrocarbyl group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbyl groups herein contain 1 to about 30 carbon atoms. Included in the meaning of "substituted" are heteroaromatic rings.

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• By an alkyl aluminum compound is meant a compound in which at least one alkyl group is bound to an aluminum atom. Other groups such as alkoxide, oxygen, and halogen may also be bound to aluminum atoms in the compound.

• By "hydrocarbylene" herein is meant a divalent group containing only carbon and hydrogen. Typical hydrocarbylene groups are $-(CH_2)_4-$, $-CH_2CH(CH_2CH_3)CH_2CH_2-$ and



(An)

If not otherwise stated, it is preferred that hydrocarbylene groups herein contain 1 to about 30 carbon atoms.

• By "substituted hydrocarbylene" herein is meant a hydrocarbylene group which contains one or more substituent groups which are inert under the process conditions to which the compound containing these groups is subjected. All of the hydrogen atoms may be substituted, as in trifluoromethyl. The substituent groups also do not substantially interfere with the process. If not otherwise stated, it is preferred that substituted hydrocarbylene groups herein contain 1 to about 30 carbon atoms. Included within the meaning of "substituted" are heteroaromatic rings.

• By an (inert) functional groups is meant a functional group that does not substantially interfere with the utility of the compound in which that group is located and does not make that compound unstable to the point where it is not useful for its intended purpose. Useful functional groups include halo and ether.

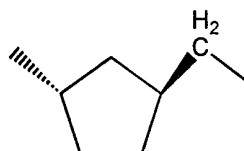
• By "anti" herein is meant that when R^5 is identical to R^{10} , and R^9 is identical to R^{14} , the

identical groups (i.e., the pairs R⁵ and R¹⁰, and R⁹ and R¹⁴ are on opposite sides of the approximate plane formed by the two carbons and the two nitrogen atoms of the α -diimine grouping and the nickel atom.

5 In the polymerization process described herein for the substituted cyclopentenes (SCP) using α -diimine complexes of nickel or palladium, the same catalysts compounds and systems and conditions as reported in World Patent Application 96/23010, which is hereby
10 included by reference, are used. Preferred nickel and palladium complexes reported therein, especially those preferred for the polymerization of cyclopentene itself, are preferred for the polymerization of the SCP reported herein. Likewise, preferred conditions, such
15 as temperature and solvent (if used) are also preferred herein. A preferred cocatalysts, as in WO 96/23010 is an alkyl aluminum compound.

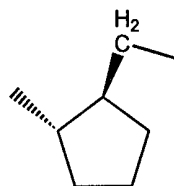
The various SCP reported herein polymerize to form one or more "unusual" repeat units in the resulting
20 polymer. Rarely if at all does any of the SCP polymerize into the polymer merely by adding across the double bond present in the cyclopentyl ring. Also, there may be a difference between repeat structures obtained using nickel and palladium complexes. The
25 structures of various polymers are described below.

• 3- and 4-Methylcyclopentene with Pd Catalyst
(see Examples 4, 5 and 8). These two monomers give almost identical polymers with Pd catalysts. The majority of the repeat units are 1,3'-trans of the
30 formula



(II),

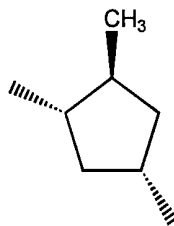
typically about 80 mole percent of the repeat units.
1,2'-Trans units,



(III)

are also present in minor amounts, typically about 10-25 mole percent of the repeat units. There may also be small amounts of repeat units containing pendant methyl groups, especially from 4-methylcyclopentene.

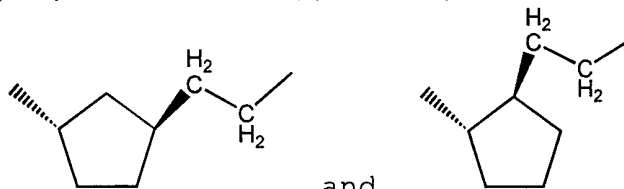
- 3-Methylcyclopentene with Ni Catalyst (Example 6). This polymerization gives polymers with substantial amounts (preferably >40 mole percent, and typically 60 mole percent) of repeat units of the formula (II). Also present are a substantial amount of repeat unit (IX), typically about 40 mole percent of the repeat units.



(IX)

- 4-Methylcyclopentene and Ni Catalyst (Example 13). This gives a polymer containing substantial amounts of repeat units (II) and (IX), typically about 50 mole percent of each.

- 3-Ethylcyclopentene with Pd Catalyst (Example 9). This polymer has two predominant structures, 1,3'-trans (IV), and 1,2'-trans (V),



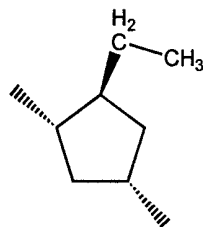
(IV)

(V)

The majority of the repeat units, typically about 75 mole percent are (IV), while a minority, usually a substantial amount, of the repeat units are (V), typically about 25 mole percent.

- 3-Ethylcyclopentene with Ni Catalyst

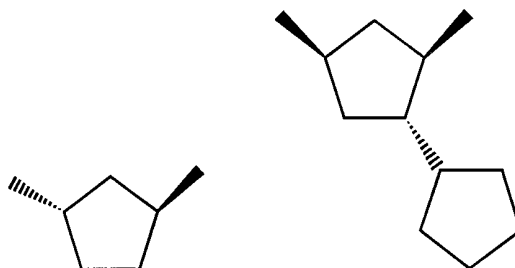
(Example 12). Structures believed to be present in substantial amounts include (IV) and (VI). Typically (IV) is a majority of the repeat units, often about 70 mole percent, while (VI) is typically about 30 mole percent of the repeat units.



(VI)

- Cyclopentylcyclopentene with Ni Catalyst

(Example 2). In this polymer, trans 1,3-cyclopentyl, (VII), is a majority of the repeat unit of the polymer, typically about 80 mole percent, while cis-1,3 enchainment (VIII) is a minor, but usually substantial, portion of the repeat units, typically about 20 mole percent.



(VII)

(VIII)

By a "substantial" amount of repeat units herein in any particular polymer is meant at least 10 mole percent of the repeat units.

The homo- and copolymers described herein are useful as thermoplastic molding resins (for those that are crystalline or glassy at ambient conditions) or as elastomers (for those which are rubbery at ambient conditions). In copolymers with cyclopentene, the use of the substituted cyclopentenes allows lowering of the melting point of the polymer, when compared to homopolycyclopentene.

It has been found that in complexes like (X), when none of R^5 , R^9 , R^{10} , and R^{14} are hydrogen, rotation about

the C-N bond of the aryl groups is hindered. Therefore, when R⁵ is the same as R¹⁰, and R⁹ is the same as R¹⁴ the complex can exist and be isolated as either syn or anti isomers. (X) is the anti form of the compound. It is preferred that R⁵, R⁹, R¹⁰, and R¹⁴ are hydrocarbyl, substituted hydrocarbyl, or halo. In another preferred embodiment, R⁵, R⁹, R¹⁰, and R¹⁴ are all alkyl and it is more preferred that R⁵ and R¹⁰ are methyl, and R⁹ and R¹⁴ are identical alkyl groups having 2 or more carbons, especially preferably R⁹ and R¹⁴ are isopropyl. It is also preferred that X is halide and/or n is 2. It is also preferred that in (X) R³ and R⁴ taken together are (An).

(X) can be made by methods described in World Patent Application 96/23010. The anti isomer may be isolated by fractional crystallization.

In the polymerization process described herein using (X), the same catalyst system and conditions as reported in World Patent Application 96/23010 for α -diimine complexes, which is hereby included by reference, are used. Preferred structures are also reported therein, especially those preferred for the polymerization of cyclopentene itself, and are also preferred for the polymerization using (X). Likewise, preferred conditions, such as temperature and solvent (if used) are also preferred herein. A preferred cocatalyst, as in WO 96/23010 is an alkyl aluminum compound.

Compounds such as (X), when polymerizing cyclopentene, give a polymer which has properties that are often different from those polymers obtained with other α -diimine nickel complexes. For example, at equivalent conditions, the melting point tends to be somewhat higher. This is believed to be due to a different mechanism of stereoregulation by these complexes compared to other nickel α -diimine complexes. Other α -diimine nickel complexes produce partially isotactic polycyclopentene by a chain end control

mechanism. (Stephan J. McLain et. al., *Macromolecules*,
Volume 31, Number 19, pages 6705-6707, 1998). By
studying the hydrooligomerization reaction by the
method described in this reference, we have found that
5 surprisingly, compounds (X) give enantiosite control of
the polymerization instead of the chain-end control of
stereochemistry observed with α -diimine Ni complexes.
We believe this mechanism of stereocontrol produces
longer isotactic segments in the partially isotactic
10 polymer, thus leading to higher melting points. If the
polymerization temperature is raised, the melting point
of polycyclopentene made by any α -diimine nickel
complex will usually decrease. It is usually desirable
to run polymerizations at higher temperatures because
15 the rates usually increase with temperature. Thus a
balance often needs to be struck between polymerization
rate and polymer melting point. An advantage of (X)
when R^3 and R^4 taken together are (An) is that it can
be used at a higher polymerization temperature and
20 still produce a polymer with a relatively high melting
point, although the polymer will have a melting point
that is lower than obtained at lower reaction
temperatures.

In the Examples, the following convention is used
25 for naming α -diimine complexes of metals, and the
 α -diimine itself. The α -diimine is indicated by the
letters "DAB". To the left of the "DAB" are the two
groups attached to the nitrogen atoms, herein often
called R^2 and R^5 . To the right of the "DAB" are the
30 groups on the two carbon atoms of the α -diimine group,
herein usually termed R^3 and R^4 . To the right of all
this appears the metal, ligands attached to the metal
and finally any anions (X).

In the Examples the following abbreviations are
35 used:

3-EtCyp - 3-ethylcyclopentene
3-MeCyp - 3-methylcyclopentene
4-MeCyp - 4-methylcyclopentene

BAF - tetrakis[3,5-
bis(trifluoromethyl)phenyl]borate

DSC: Differential Scanning Calorimetry

H_f - heat of fusion (melting)

5 MeOH - Methanol

PMAO - polymethylaluminoxane

RT - room temperature

TCB - 1,2,4-trichlorobenzene

Tg - glass transition temperature

10 TGA - thermogravimetric analysis

Tm - melting point

NMR Techniques

The following describes generally some of the
techniques used in determining the structures of the
15 polymers described herein.

INADEQUATE (Incredible Natural Abundance Double QUantum
Transfer Experiment):

This 2D NMR technique gives information on
connectivities between carbon atoms. The 2D contour
20 map shows correlations between carbons and their double
quantum frequencies. Carbons which share the same
double quantum frequency (have correlations on the same
ROW of the 2D plot) are connected by covalent bonds.
This is a ¹³C observe experiment with VERY LOW signal
25 to noise, and can take 4 days per sample.

HMQC (Heteronuclear Multiple Quantum Coherence):

This 2D NMR technique gives information on
connectivities between carbons and protons that are
directly bonded to each other. The correlations in the
30 2D contour plot connect each proton signal with the
carbon signal for the carbon covalently bonded to that
proton. This is a high signal-to-noise very quick ¹H
NMR observe experiment. The digital resolution is best
in the ¹H dimension.

35 HSQC (Heteronuclear Single Quantum Coherence):

The 2D NMR experiment gives basically the same
results as the HMQC experiment, but is sometimes better

for polymers which have shorter relaxation time constants.

HETCOR (HETeronuclear CORrelation):

This 2D NMR technique gives information on connectivities between carbons and protons that are directly bonded to each other. The correlations in the 2D contour plot connect each carbon signal with the proton signal for the proton covalently bonded to that carbon. This is a low signal-to-noise ^{13}C observe experiment. The digital resolution is best in the ^{13}C dimension.

HMBC (Heteronuclear Multiple Bond Correlation):

This 2D NMR technique gives information on connectivities between carbons and protons that are separated by two and/or three covalent bonds. The correlations in the 2D contour plot connect each proton signal with the carbon signal for the carbons that are two and/or three bonds separated from that proton. This is a medium signal-to-noise ^1H NMR observe experiment and requires magnetic field gradients to be really successful. The digital resolution is best in the ^1H dimension. The carbon does not need to carry a proton, making this a useful adjunct to the HMQC-TOCSY experiment.

TOCSY (TOtal Correlation SpectroscopY):

This 2D NMR technique gives information on all the protons in a particular neighborhood. How big the neighborhood is depends on the length of the NMR spin lock that is used in the experiment, and can be adjusted. The neighborhood encompasses a group of protons that are pairwise on neighboring carbons and are pairwise spin coupled to each other. A quaternary carbon, ether, carbonyl, etc., interrupts the chain of protons on neighboring carbons and limits the neighborhood. This is a high signal to noise ^1H observe experiment.

HMQC-TOCSY (or HSQC-TOCSY)

This experiment combines the HMQC (or HSQC) and TOCSY experiments together. The result is that each proton shows correlations to all the protonated carbons in its neighborhood, thus defining a GROUP of carbons that are pairwise covalently bonded. This is a medium signal-to-noise ^1H NMR observe experiment. The digital resolution is best in the ^1H dimension. This is one of the most useful experiments as it groups both the protons and carbons that belong in a particular area or microstructure of the polymer.

COSY (COrrrelation SpectroscopY):

This 2D NMR technique gives information on protons that are spin coupled to each other, generally on neighboring carbons or 4 bonds apart. This is a high signal-to-noise very quick ^1H NMR observe experiment.

DEPT (Distortionless Enhancement by Polarization Transfer):

This 1 D multipulse NMR experiment gives information on the number of protons attached to each carbon atom. Carbons with one or three protons attached are positive, carbons with two protons attached are negative, and carbons without any protons are not observed in this experiment. This is a ^{13}C observed experiment, but the signal to noise is very high because magnetization is transferred from the protons and because the scans can be repeated according to the proton (not the carbon, which is slower) relaxation time.

Melting points

The melting point of the polymers, particularly homopolycyclopentene, are determined by Differential Scanning Calorimetry at a heating rate of $15^\circ\text{C}/\text{min}$ (except as otherwise noted, but this rate is the rate applicable in the claims - lower heating rates tend to give somewhat lower melting points, and higher heating rates tend to give somewhat lower melting points), and taking the maximum of the melting endotherm as the melting point. However these polymers tend to have

relatively diffuse melting points, so it is preferred to measure the "melting point" by the end of melting point. The method is the same, except the end of melting is taken as the end (high temperature end) of the melting endotherm which is taken as the point at which the DSC signal returns to the original (extrapolated) baseline. If not stated as an end of melting point the melting point has been taken as the peak of the melting endotherm.

10 Monomer Sources

3-Methylcyclopentene (3-MeCyp); prepared according to Nugent et. al. (J. Am. Chem. Soc., 1995, vol. 117, p. 8992) was degassed and stored in a drybox over 5Å molecular sieves.

15 3-Ethylcyclopentene (3-EtCyp) (Wiley Organics, 99%) was degassed and taken into a nitrogen purged drybox. It was then run through alumina and stored over 5Å molecular sieves.

4-Methylcyclopentene (4-MeCyp) (Carnegie Mellon University-American Petroleum Institute standards) was used as received.

Cyclopentylcyclopentene was obtained from Chemsampco.

Example 1

25 Preparation of Poly(cyclopentene-co-3-Ethylcyclopentene)

In a dry box, to an oven dried scintillation vial, were added in order: (XIII) (0.04 g, 0.06 mmol); tris(perfluorophenyl)borane (0.094 g, 0.184 mmol); cyclopentene (2.08 g, 30.5 mmol); 3-ethylcyclopentene (2.92 g, 30.4 mmol) and then triethylaluminum (1.0 M in hexanes, 183 µl, 0.183 mmol). The reaction exothermed initially and the viscosity increased within one h. The reaction was mixed on the IKA Vibrax-VXR® mixer for 17 h total after which time a solution of toluene (8 ml) and 8-hydroxyquinoline (0.05 g, 0.34 mmol) was added and the mixture was allowed to stand overnight. The mixture was removed from the scintillation vial and

stirred with an additional 30 ml of toluene to completely dissolution in a small Erlenmeyer flask for 2 h. The mixture was then precipitated into 500 ml of MeOH, filtered, washed with MeOH and dried on the vacuum line at 110°C for 4 h. Net wt = 2.87 g. By DSC (heating rate of 30 °C/min) the polymer had a Tg at 58°C and no melting transition.

Example 2

Preparation of Poly(3-Cyclopentylcyclopentene)

10 In a dry box, to an oven dried scintillation vial, were added in order: (XIII) (0.024 g, 0.036 mmol); tris(perfluorophenyl)borane (0.056 g, 0.109 mmol); 3-cyclopentylcyclopentene (2.46 g, 18.1 mmol) and then triethylaluminum (1.0 M in hexanes 109 µl, 0.109 mmol)

15 The reaction was mixed on the IKA-Vibrax-VXR® vibramixer for 70 h, at the end of which the reaction mixture was immobile. At 70 h, 8-hydroxyquinoline (0.106 g, 0.726 mmol) and toluene (8.8 ml) were added to quench the reaction and mixed for 2 h. Not all of

20 the polymer dissolved during this period. The reaction was dumped into 50 ml of stirred MeOH, filtered and washed with 3 X 20 ml of fresh MeOH. This polymer was then re-dissolved in 20 ml of chlorobenzene at 120°C and reverse precipitated upon cooling by the slow

25 addition of MeOH (60 ml) to the stirred solution of polymer. The polymer precipitated as a blob. The cloudy supernatant was decanted and the elastomeric solid was slurried and kneaded in 3 portion (15 ml) each of MeOH. The wash supernatant was decanted off

30 the polymer following each kneading. The polymer was dried overnight in the dry box antechamber and then at 125°C on a vacuum line for 4 h. Net wt. = 1.17 g. By DSC (heating rate 30°C/min) the polymer had a Tg of 70°C.

Example 3Preparation of Poly(Cyclopentene-co-3-ethylcyclopentene)

In a dry box, to an oven dried scintillation vial,
5 were added in order: (XIII) (0.0095 g, 0.014 mmol);
tris(perfluorophenyl)borane (0.022 g, 0.043 mmol);
cyclopentene (9.34 g 137 mmol); 3-ethylcyclopentene
(0.66 g, 6.86 mmol) and then triethylaluminum (1.0 M in
hexanes, 43 μ l, 0.043 mmol). The reaction was mixed
10 on the IKA-Vibrax-VXR® vibramixer for 96 h after which
methylene chloride (1 ml) and 8-hydroxyquinoline (0.043
g, 0.29 mmol) were added to quench the reaction. The
reaction was then poured into 50 ml of stirred MeOH,
filtered and washed with 3 X 20 ml of MeOH. The solid
15 was dried overnight at 120°C in a vacuum oven with a
slow nitrogen bleed. Net wt. = 1.53 g.

Example 43-Methylcyclopentene Polymerization with Pd catalyst.

Inside a nitrogen purged drybox, the palladium
20 catalyst, $\{[(2,6\text{-iPr}_2\text{Ph})_2\text{DABMe}_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\}\text{BAF}$
(46 mg, 0.031 mmol), was dissolved in 1 ml anhydrous
 CH_2Cl_2 . 3-MeCyp (1 ml) was added and the resulting
solution allowed to stir for 7 days over which time it
gradually darkened. The volatile solvent and unreacted
25 monomer were removed and the resulting sticky polymer
was washed with MeOH and dried. $T_g = 10^\circ\text{C}$ (DSC)

Example 53-MeCyp Polymerized with a Pd Catalyst

Inside a nitrogen purged drybox, the palladium
30 catalyst, $\{[(2,6\text{-iPr}_2\text{Ph})_2\text{DABMe}_2]\text{Pd}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})\}\text{BAF}$
(0.020 g, 0.014 mmol), was dissolved in anhydrous
 CH_2Cl_2 (1 ml) and 3-MeCyp (1.25 ml) was added. The
resulting solution was stirred for 2 h after which it
had become viscous. After 4 h it had solidified and
35 stopped stirring. The solution was allowed to react
for a further 5 days after which the solvent and
volatiles were removed and the resulting foam dried
under vacuum overnight. Yield = 0.72 g.

Example 63-MeCyp Polymerized with a Ni Catalyst

Inside a nitrogen purged drybox, the nickel catalyst, [(2,4,6-Me₃Ph)₂DABAN]NiBr₂ (0.010 g, 0.015 mmol) was placed in anhydrous toluene (1 ml) and 3-MeCyp (1.25 ml) added. PMAO (1.1 ml, 9.8wt% Al in toluene, Akzo) was added with stirring and the resulting deep purple solution was stirred for 5 days. It was then removed from the drybox and MeOH/10%HCl added. The sticky polymer precipitated and the solvents were decanted. The polymer was washed repeatedly with MeOH with stirring until a fine powder formed. This was filtered and washed and dried.

Example 715 Cyclopentene/3-Methylcyclopentene Copolymer.

Inside a nitrogen purged drybox, the palladium catalyst, {[(2,6-iPr₂Ph)₂DABMe₂]Pd(CH₂CH₂CH₂CO₂Me)}BAF (77 mg, 0.053 mmol) was dissolved in CH₂Cl₂ (2 ml) and cyclopentene (2 ml) and 3-MeCyp (1 ml) added. The solution was stirred for 4 days after which the volatiles were removed. MeOH was added and the polymer filtered, washed well with MeOH and finally with 2% Irganox® 1010/acetone solution and dried. Yield = 1.06 g. T_m (DSC) = 210.5°C, T_g (DSC) = 73°C. ¹³C-NMR (TCB, 120°C) indicated ~5% 3-MeCyp incorporation.

Example 84-Methylcyclopentene Polymerization with Pd catalyst.

Inside a nitrogen purged drybox, the palladium catalyst {[(2,6-iPr₂Ph)₂DABMe₂]Pd(CH₂CH₂CH₂CO₂Me)}BAF (20 mg, 0.031 mmol) was dissolved in 1 ml CH₂Cl₂. 4-MeCyp (1 ml) was added and the resulting solution allowed to stir for 5 days over which time it gradually darkened. The volatile solvent and unreacted monomer were removed resulting in a sticky orange foam (0.25 g).

Example 93-Ethylcyclopentene Polymerized with a Pd Catalyst

Inside a drybox, the palladium catalyst,
{[(2,6-*i*Pr₂Ph)₂DABMe₂]Pd(CH₂CH₂CH₂CO₂Me)}BAF (24 mg,
5 0.016 mmol) was dissolved in anhydrous dichloroethane
(2 ml) and 3-EtCyp (1.58 g) was added. The orange
solution was stirred at room temperature and after 12 h
had solidified. After 8 days the volatiles were
removed. The polymer was removed from the drybox and
10 MeOH was added and the polymer filtered, washed well
with MeOH and finally with 2% Irganox® 1010/acetone
solution and dried. Yield = 1.06 g. No crystallinity
was observed in the DSC analysis.

Example 103-Ethylcyclopentene Polymerized with a Ni Catalyst

Inside a drybox, the nickel catalyst,
[(2-PhPh)₂DABMe₂]NiBr₂ (10.8 mg, 0.018 mmol) was placed
in anhydrous toluene (2 ml) and 3-EtCyp (1.72 g) was
added. PMAO (0.5 ml, 9.8wt% Al in toluene, Akzo) was
20 added with stirring and the resulting deep purple
solution was stirred for 8 days. It was then removed
from the drybox and MeOH/10%HCl added. The organic
layer was isolated and the volatiles removed. This was
washed successive times with MeOH and then dried.
25 Yield = 0.43 g of a viscous oil.

Example 113-Ethylcyclopentene Polymerized with a Ni Catalyst

Inside a drybox, the nickel catalyst,
[(2,4,6-Me₃Ph)₂DABAN]NiBr₂ (16.5 mg, 0.026 mmol) was
30 placed in a glass vial and 3-EtCyp (2.5 g) was added.
B(C₆F₅)₃ (40 mg, 0.08 mmol) and AlEt₃ (0.08 ml, 0.08
mmol) were added with stirring and the resulting deep
purple solution was stirred for 8 days. At this time
it was solidified. It was removed from the drybox and
35 dissolved in CH₂Cl₂ and precipitated by addition to
MeOH. The product was filtered, washed well with MeOH
and dried under vacuum. Yield = 2.27 g. TGA shows no

weight loss up to 400°C. Tg (DSC) 11.3°C. No melting point was observed by DSC.

Example 12

3-Ethylcyclopentene Polymerization with a Ni Catalyst

5 Inside a drybox, the nickel catalyst,
[(2-PhPh)₂DABMe₂]NiBr₂ (15.8 mg, 0.026 mmol) was placed
in a glass vial and 3-EtCyp (2.5 g) was added. B(C₆F₅)₃
(40 mg, 0.08 mmol) and AlEt₃ (0.08 ml, 0.08 mmol) were
added with stirring and the resulting deep brown
10 solution was stirred for 8 days. At this time it was
viscous. It was removed from the drybox, dissolved in
CH₂Cl₂ and precipitated by addition to MeOH. The
liquid was decanted and washed repeatedly in this way
with MeOH and finally dried under vacuum. Yield =
15 1.83 g viscous oily polymer. TGA shows no weight loss
up to 350°C. Tg (DSC) 1.9°C. No melting point was
observed by DSC.

Example 13

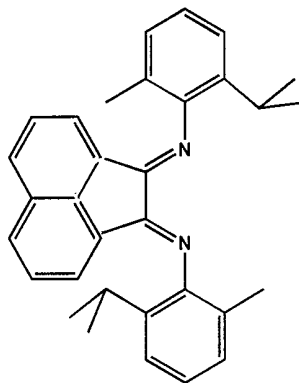
4-Methylcyclopentene Polymerized with a Ni Catalyst

20 Inside a drybox, the nickel catalyst,
[(2,4,6-Me₃Ph)₂DABAN]NiBr₂ (9.8 mg, 0.015 mmol) was
placed in a glass vial with anhydrous toluene (2 ml)
and 4-MeCyp (1 ml) was added. PMAO-IP (0.8 ml, 12.8wt%
Al in toluene, Akzo) was added with stirring and the
25 resulting deep purple solution was stirred for 10 days.
At this time it was viscous. It was removed from the
drybox and MeOH/10% HCl was added to precipitate the
polymer. It was then redissolved in CHCl₃ and
precipitated by addition to MeOH. The product was
30 filtered, washed well with MeOH and dried under vacuum.
Yield = 0.41 g white solid. Tg (DSC) = 40.8°C. No
melting point was observed in the DSC.

Example 14

35 To a 3-necked 250 RBF equipped with a condenser,
stoppers and a magnetic stir bar is charged (3.0 g, 16
mmol) of acenaphthenequinone, (5.6 g, 38 mmol) of
2-methyl-6-isopropylaniline and 40 ml of glacial acetic
acid. The reaction was placed under a N₂ blanket and

heated to reflux for 30 min. The reaction was cooled to room temperature over 45 min, and a red orange solid precipitated from solution. The solid was filtered and washed with 20 ml of glacial acetic acid followed by 2 x 25 ml of MeOH. The solid was dried at room temperature for 50-60 h under vacuum to yield (3.61 g, 8.12 mmol, 50.7 % yield) of

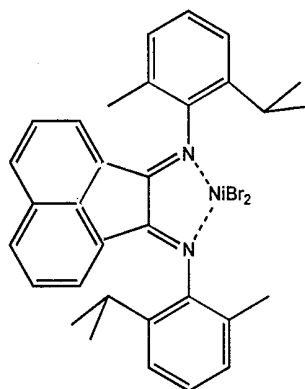


(XII)

¹H NMR (500 MHz, CD₂Cl₂, ppm downfield of TMS): 0.98 (d, CHMe₂, 6H), 1.21 (d, CHMe₂, 6H), 2.06, 2.10 (CH₃, anti isomer (major) and syn isomer (minor), 6H), 3.00 (m, CHMe₂, 2H), 6.5 - 8.3 (multiple peaks for aromatic protons, 12H).

Example 15

In a dry box, to a one liter RBF, was charged (2.01 g 4.52 mmol) of (XII), (0.697 g, 2.26 mmol) of NiBr₂·1,2-dimethoxyethane complex and 26 ml anhydrous methylene chloride. This mixture was stirred for 1.5 h at room temperature. The methylene chloride was then evaporated to leave a brick red solid residue. The solid was collected and charged to a Soxhlet extractor and extracted with pentane for 4 h to remove excess (XII). The resulting greenish solid was dried overnight under vacuum at room temperature to yield (1.17 g, 1.76 mmol, 78.1 % yield) of crude



(XIII)

Crude (XIII) (1.17 g) was taken up in 50 ml of anhydrous methylene chloride to which was added 50 ml of anhydrous pentanes. This solution became slightly cloudy. This solution was filtered through a fine fritted funnel into a 125 ml Erlenmeyer flask. The flask was stoppered and allowed to stand overnight at room temperature over which time crystallization occurred. The crystallized solid was filtered and washed with 3 x 20 ml portions of diethyl ether. This product was dried overnight under vacuum to yield 0.87 g of greenish, finely divided crystalline solid.

The finely divided crystalline solid (0.87 g) was dissolved in 14 ml of anhydrous methylene chloride. To this mixture is added 8.5 g of pentane at once, and then, slowly 2 additional g of pentane to the point of solution turbidity. This solution was allowed to stand overnight at room temperature in the dry box over which time greenish, yellow crystals formed. This solid was filtered and dried for 4 h under vacuum to yield the anti form of (XIII) (0.55 g, 0.83 mmol, 36.7 % overall yield). ^1H NMR (500 MHz, CD_2Cl_2 , ppm downfield of TMS): -15.351 (s, para-ArH, 2H), 2.868 (s, CHMe_2 , 6H), 3.556 (s, CHMe_2 , 6H), 5.958 (d, $J = 4.0$ Hz, acenaphthene ArH, 2H), 13.177 (broad s, CHMe_2 , 2H), 16.952 (d, $J = 6.0$ Hz, acenaphthene ArH, 2H), 22.525 (s, ArH, 2H), 22.917 (s, ArH, 2H), 23.692 (s, o- CH_3 , 6H), 25.047 (s, ArH, 2H).

Example 16

In a dry box, to an oven dried Schlenk flask, was charged of cyclopentene (10 g, 147 mmol) and anti-

(XIII) (0.01 g, 0.015 mmol). The Schlenk flask was sealed and placed in a drybox freezer and chilled over 40 min to -24°C. At -24°C, triethylaluminum (44 μ l 1M in hexane, 0.044 mmol) and tris(perfluorophenyl)borane (0.023 g, 0.045 mmol) were added to the flask. The Schlenk flask was immediately resealed and removed from the drybox and placed into a 0°C bath and mixed for 96 h under N₂ during which time a solid precipitate formed. After 96 hrs, 8-hydroxyquinoline (0.02 g, 0.138 mmol) was added to the reaction mixture. The reaction was allowed to stir and warm to room temperature over 20 min after which time the precipitated solid was filtered and washed on the filter with 3 X 30 ml of MeOH. The filtered solid was dried under vacuum to yield 0.26 g of tan solid.

Example 17

In a dry box, to an oven dried Fisher-Porter tube, was charged of cyclopentene (10 g, 147 mmol) and anti-(XIII) (0.01 g, 0.015 mmol), triethylaluminum (44 μ l 1M in hexane, 0.044 mmol), and tris(perfluorophenyl)borane (0.023 g, 0.045 mmol). The tube was sealed and immediately removed from the drybox and placed into a 50°C oil bath for 16 h where it was mixed until it became immobile. After 16 h the Fisher-Porter tube was removed from the oil bath and cleaned thoroughly on the outside and broken to remove the polymer. The polymer was cut into smaller pieces and placed into a Waring® Blender. The blender was charged with 300 ml of MeOH and 8-hydroxyquinoline (0.02 g, 0.138 mmol) and then run at high speed for 30 min. The solid from the blender was collected on a filter and dried under vacuum at room temperature for 2 days to yield 5.65 g of solid. The end of the polymer melting transition occurred at about 325°C.

Example 18

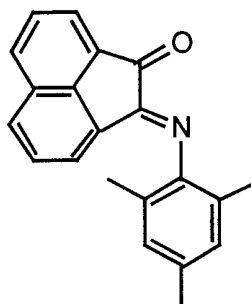
In a nitrogen filled dry box, to an oven dried scintillation vial (Vial A) equipped with a magnetic stir bar was added (XIII) (0.0097 g, 0.0146 mmol). To

a separate oven dried scintillation vial (Vial B) was added perfluorotriphenyl borane (0.023 g, 0.045 mmol), 10 g of cyclopentene (146.8 mmol) and, 23 μ l of triethylaluminum (1.9 M in toluene, 0.045 mmol). After
5 thoroughly mixing vial B to dissolve the borane, the contents of vial B were added to vial A and the mixture was shaken on a Vibramixer® for 168 h at RT. After 168 h of vigorous mixing, 1 ml of methanol was added to the vial to quench the reaction. After 10 min of
10 additional mixing the entire reaction mixture was added to 50 ml of aqueous concentrated HCl/MeOH (3% v/v) and further mixed for 15 min. The solid precipitate was filtered on a medium fritted glass filter and washed with methanol followed by an Irganox 1010®/acetone
15 solution (2 % wt/wt). The solid was then dried overnight in vacuo. Net dry weight = 3.23 g. The end of the polymer melting transition as measured by DSC (30°C per minute) occurred at approximately 358°C.

Example 19

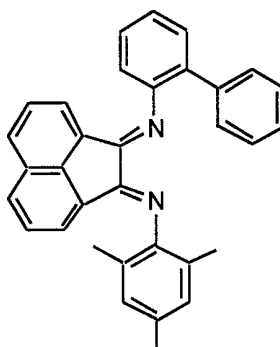
Preparation of (XV)

20 Acenathaquinone (15 g, 82 mmol), 2,4,6-trimethylaniline (2.21 g, 16.4 mmol) and formic acid (0.15 g) were combined in 450 mL of anhydrous methanol. The mixture was stirred at room temperature
25 for 60 h under nitrogen, and then evaporated to dryness on a rotoevaporator. The residue was stirred with 450 mL of refluxing ethyl acetate for 30 min and allowed to cool to RT. The mixture was filtered and the filtrate was evaporated to give 4.3 g of red orange solid. This
30 solid was purified by flash chromatography on silica gel with hexane/ethyl acetate (3:1) to give 3.9 g of monoimine (XIV) as an orange crystalline solid (80% yield based on 2,4,6-trimethylaniline).



(XIV)

¹H NMR (300 MHz, CDCl₃): 2.2 (s, o-CH₃, 6H); 2.6 (s, p-CH₃, 3H); 6.9-8.6 (m, ArH, 8H). The monoimine (XIV) (1.796 g, 6 mmol) was combined with 20 mL of anhydrous methanol and two drops of formic acid in a 500 mL round-bottom flask. o-Phenylaniline (0.20 g, 1.2 mmol) was added to this heterogeneous mixture, and the reaction was stirred at RT for 24 h under a nitrogen atmosphere. The reaction mixture was evaporated to dryness on a rotoevaporator. The orange residue was flash chromatographed on silica gel using a 3:1 mixture of hexane/ethyl acetate (3:1). The desired product (XV)



(XV)

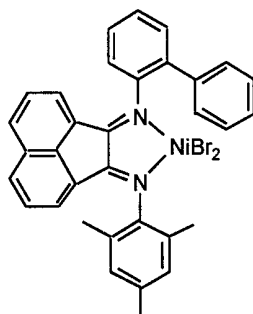
15

(0.285 g yellow solid) was eluted immediately after a faster eluting side-product. It was recrystallized from 5 mL of hexane at -30°C to give 0.130 g (24% yield based upon monoimine XIV). ¹H NMR (300 MHz, CD₂Cl₂): 1.80, 1.98 (s, s o-CH₃, 6H); 2.29, 2.37 (s, s, p-CH₃, 3H); 6.55-8.2 (m, ArH, 17H). Based on the small extra methyl resonances at 1.80 and 2.29, there appear to be two isomers in a ratio of 85:15.

20

Example 20Preparation of (XVI)

(XV) (0.050 g, 0.111 mmol) and NiBr₂(1,2-dimethoxyethane) (0.034 g, 0.111 mmol) were combined in 1.7 mL of CH₂Cl₂ in a glass vial and shaken on a vibrating mixer for 24 h in a nitrogen filled drybox. The solution was filtered through a 0.45 μm PTFE membrane filter and the solvent was removed in vacuo to give a rust-brown solid. The product was washed with pentane (2 x 3 mL) and dried at room temperature in vacuo to give 0.065 g (88% yield). A portion of the sample was recrystallized from toluene/pentane (1:1) by adding pentane slowly to a filtered toluene solution until it became turbid, and then cooling to -30°C overnight to give dark purple crystals of (XVI).



(XVI)

Anal. found (calcd. for C₃₃H₂₆Br₂N₂Ni): C, 59.76 (59.24); H, 4.41 (4.19); N, 4.35 (3.92).

20

Example 21

In a nitrogen filled dry box, to an oven dried scintillation vial (Vial A) equipped with a magnetic stir bar was added (XVI) (0.0098 g, 0.0146 mmol). To a separate oven dried scintillation vial (Vial B) was added perfluorotriphenyl borane (0.0225 g, 0.045 mmol), 10 g of cyclopentene (146.8 mmol) and, 23 μl of triethylaluminum (1.9 M in toluene, 0.045 mmol). After thoroughly mixing vial B to dissolve the borane, the contents of vial B were added to vial A. Half of this mixture was shaken on a Vibramixer® for 72 h at RT, and then quenched by addition of 3 mL of MeOH. After 10 min of additional mixing the entire reaction mixture

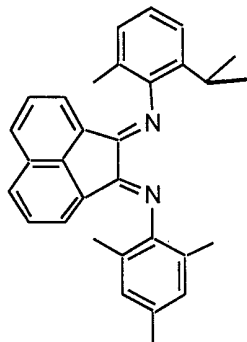
30

was added to 50 ml of conc. aqueous HCl/MeOH (3% v/v) and mixed for 15 min. The solid precipitate was filtered on a medium fritted glass filter and washed with methanol followed by an Irganox[®] 1010/acetone solution (2% wt/wt). The solid product was then dried overnight in vacuo. Net dry weight = 0.80 gm. The end of the polymer melting transition as measured by DSC (30°C per min) occurred at approximately 380°C.

Example 22

10 Preparation of (XVII)

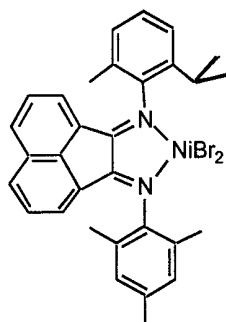
In a nitrogen filled dry box to an oven dried scintillation vial was charged mono-imine (XIV) (0.6 g, 2.0 mmol), 20 ml of methanol and 2-isopropyl-6-methyl aniline (0.06 g, 0.40 mmol). The reaction was catalyzed with the addition of 2 drops of formic acid (~0.4 mmol). The mixture was sealed and stirred for 6 days at RT. After 6 days the entire mixture was evaporated to dryness in the presence of 2.0 g of silica gel 60. This silica gel was subjected to column chromatography on silica gel using 75/25 (v/v) hexane/ethyl acetate. The product band was visible in the column and was the first fraction collected. TLC in 75/25 (v/v) hexane/ethyl acetate shows this residue to be a mixture of compounds with one major constituent. This fraction was evaporated to dryness and analyzed by ¹H NMR which confirmed the product to be a mixture with the major component being the desired ligand (XVII).



(XVII)

Example 23Preparation of (XVIII)

In a nitrogen filled drybox, to an oven dried scintillation vial were added (XVII) (0.135 g, 0.314 mmol), 4.7 mL of anhydrous methylene chloride and NiBr₂(1,2-dimethoxyethane) (0.097 g, 0.314 mmol). The vial was sealed and stirred for 4 h. After 4 h the solvent was removed under vacuum in the drybox. The solid was then washed with 3 X 10 ml of pentane by slurring in the scintillation vial, allowing the solid to settle and then decanting the supernatant pentane away via pipette. The product (XVIII) was dried overnight in vacuo.



(XVIII)

15

Example 24

In an nitrogen filled dry box, to an oven dried scintillation vial were added (XVIII) (0.0094 g, 0.0145 mmol), perfluorotriphenyl borane (0.023 g, 0.045 mmol) and cyclopentene (10 g, 146.8 mmol). This mixture was shaken vigorously for 10 min to dissolve the borane. After borane solvation, 44 μ l of triethylaluminum was added (1.0 M in hexane 0.044 mmol) and the mixture was further shaken for 30 min where-by a slight pink haze began to develop. At this point a 5 gm aliquot (50% of the mixture) was removed and placed in a separate scintillation vial and mixed by shaking for 168 h. The mixture was then quenched by the addition of 1 mL of MeOH. After 10 min of additional mixing the entire reaction mixture was added to 50 ml of concentrated aqueous HCl/MeOH (3 % v/v) and further mixed for 15 min. The solid precipitate was filtered on a medium

fritted glass filter and washed with 3 X 20 mL of methanol followed by 20 ml of Irganox[®] 1010/acetone solution (2% wt/wt). The solid was then dried overnight in the drybox in vacuo. Net dry weight =
5 1.19 g. The end of the polymer melting transition as measured by DSC (30°C per minute) occurred at approximately 350°C.

Example 25

In a nitrogen filled drybox, to an oven dried
10 scintillation vial were added in order: (XIII) (0.0086 g), perfluorotriphenyl borane (0.020 g), cyclopentene (6.22 g), 3-ethylcyclopentene (3.78 g), and triethylaluminum (39.2 µl of a 1M solution in hexanes). The mixture was shaken at room temperature on a
15 vibrating mixer for 15.5 h and then quenched by the addition of 0.045 g 8-hydroxyquinoline dissolved in toluene. The quenched mixture was poured into 150 mL of MeOH and stirred for 3 days. The mixture was filtered and the solid product was collected on a
20 medium fritted glass filter and washed on the filter with 3 X 30 mL of additional MeOH. The solid product was dried on a high vacuum line at 111 °C for 5 hours. Yield is 1.98 g. ¹³C NMR shows that the product contains about 5 mole % 3-ethylcyclopentene. DSC
25 (30°C/min) shows an end of melting point at about 245°C. This can be compared to an end of melting point of 358°C for homopolycyclopentene made with this catalyst at RT (Example 18).

Example 26

30 Norcamphorquinone was prepared by oxidation of norcamphor using selenium dioxide following the procedure of K. Alder, et. al. Liebigs Ann. Chem. 593, 23 (1955) and used without further purification due to its instability.

35 Norcamphorquinone (4.2 g, 34 mmol) and 2-isopropyl-6-methylaniline (14.3 g, 96.2 mmol) were dissolved in 40 mL methanol. The solution was stirred at room temperature for 2 days. Thin-layer

chromatography (silica, 50 % ethyl acetate/hexanes) showed only two spots near the elution front. The solution was evaporated on a rotoevaporator to give a viscous brown oil, which was eluted through a column of basic alumina using dichloromethane to remove dark-colored material. The solution was evaporated on a rotoevaporator to give a crude orange-yellow oil, bis(2-isopropyl-6-methylphenylimino)norbornane, (2,6-iPrMePhN)₂NB, which was dried under vacuum.

10

Example 27

Inside a dry box, crude (2,6-iPrMePhN)₂NB from Example 25 (0.63 g, 1.6 mmol), and (1,2-dimethoxyethane)nickel(II) bromide (0.50 g, 1.6 mmol) were combined in 50 mL dichloromethane and stirred overnight. The solution was diluted with petroleum ether to precipitate a brown powder. The powder was collected by vacuum filtration, dissolved in minimal dichloromethane (20 mL), and diluted sequentially with petroleum ether to induce recrystallization. The crystals were collected by vacuum filtration and dried under vacuum to give 0.06 g of [(2,6-iPrMePhN)₂NB]NiBr₂.

15

20

Example 28

A sample of the oil from Example 1 was dissolved in methanol and diluted dropwise with water. An oil separated from the solution. The oil was taken up in 200 mL hexanes and extracted repeatedly with water. The solution was evaporated on a rotoevaporator and the resulting oil was dried under vacuum. The ¹H NMR (500 MHz, CDCl₃) spectrum of the oil indicated a mixture of [(2,6-iPrMePhN)₂NB and residual excess 2-isopropyl-6-methylaniline.

25

30

A sample of this oil (0.94 g) was dissolved in 15 mL glacial acetic acid and treated with 1.5 mL acetic anhydride. Nickel(II) bromide (0.44 g, 2.0 mmol) was added and the mixture was stirred for several days. The solids were collected by vacuum filtration, washed two times with acetic acid to give colorless washings,

35

washed two times with hexanes, and dried under vacuum. The solids were dissolved in dichloromethane and the solution was filtered to leave behind a dark insoluble material. The solution was diluted with sufficient
5 hexane to precipitate the solids. After filtration, a second crop was obtained by concentrating the filtrate. The combined solids were dissolved in minimal dichloromethane. The solution was slowly diluted with hexanes to induce recrystallization. The red-brown
10 crystals were collected by filtration, washed with hexanes, and dried under vacuum to give 0.59 g (48 %) of [(2,6-iPrMePhN)₂NB]NiBr₂.

Example 29

Inside a dry box, a sample of [(2,6-
15 iPrMePhN)₂NB]NiBr₂ from Example 27 (0.0070 g, 0.012 mmol) was weighed out into a glass vial. Cyclopentene (11 mL, 10,000 equivalents/Ni) was added by syringe. The polymerization was initiated with stirring by adding a 1.9 M solution of triethylaluminum in toluene
20 (0.040 mL, 6 equivalents/Ni) and tris(pentafluorophenyl)borane (0.040 g, 6 equivalents/Ni). Sufficient polymer precipitated over the course of polymerization that stirring was not maintained for the entire time. After 7 days, the
25 polymerization was quenched by adding 8-hydroxyquinoline (57 mg, 0.39 mmol) in toluene. The polymer was dispersed in a blender with 250 mL toluene. The yellow-green catalyst residues were extracted by diluting with 250 mL methanol. The polymer was
30 filtered off and washed with methanol until the filtrate was colorless, then treated with a 0.5% solution of Irganox[®] 1010 in acetone. The polymer was dried at 120°C in a nitrogen-purged vacuum oven to give 3.49 g (4400 turnovers/Ni) polycyclopentene. DSC
35 (0-350 °C, 10°C/min, second heat): T_g 101°C, T_m (onset) 114°C, T_m (peak) 232°C, T_m (end) 324°C, H_f 35 J/g. GPC (1,2,4-TCB, 135°C, IR detection, polyethylene

calibration): M_n 31,400, M_w 59,400, M_w/M_n 1.90, M_z 97,300, M_z/M_w 1.64.

Example 30

Inside a dry box, a sample of [(2,6-
5 iPrMePhN)₂NB]NiBr₂ from Example 28 (0.015 g, 0.025 mmol) was weighed out into a glass vial. Cyclopentene (22 mL, 10,000 equivalents/Ni) was added by syringe. The polymerization was initiated with stirring by adding a 1.9 M solution of triethylaluminum in toluene
10 (0.079 mL, 6 equivalents/Ni) and tris(pentafluorophenyl)borane (0.077 g, 6 equivalents/Ni). Sufficient polymer precipitated over the course of polymerization that stirring was not maintained for the entire time. After 7 days, the
15 polymer was dispersed in a blender with 200 mL toluene and 8-hydroxyquinoline (57 mg, 0.39 mmol). The yellow-green catalyst residues were extracted by diluting with 200 mL methanol. The polymer was filtered off and washed with methanol until the filtrate was colorless,
20 then treated with a 0.5% solution of Irganox[®] 1010 in acetone. The polymer was dried at 120°C in a nitrogen-purged vacuum oven to give 4.86 g (2900 turnovers/Ni) polycyclopentene. DSC (0-350°C, 10°C/min, second heat): T_g 105°C, T_m (onset) 124°C, T_m (peak) 256°C, T_m (end) 329°C, H_f 37 J/g. The polymer melting point was
25 too high to obtain a melt index or perform the molecular weight analysis.

Example 31

Inside a dry box, a sample of
30 [(2,6-iPrMePhN)₂NB]NiBr₂ from Example 28 (0.016 g, 0.026 mmol) and tris(pentafluorophenyl)borane (0.077 g, 6 equivalents/Ni) were weighed out into a glass vial. Cyclopentene (22 mL, 10,000 equivalents/Ni) was added by syringe. The polymerization was initiated with
35 stirring by adding a 1.9 M solution of triethylaluminum in toluene (0.079 mL, 6 equivalents/Ni). Sufficient polymer precipitated over the course of polymerization such that stirring was not maintained for the entire

time. After 7 days, the polymer was dispersed in a blender with 200 mL toluene and 8-hydroxyquinoline (60 mg, 0.39 mmol). The yellow-green catalyst residues were extracted by diluting with 200 mL methanol. The polymer was filtered off and washed with methanol until the filtrate was colorless, then treated with a 0.5% solution of Irganox[®] 1010 in acetone. The polymer was dried at 120°C in a nitrogen-purged vacuum oven to give 9.28 g (5200 turnovers/Ni) polycyclopentene. DSC (0-350 °C, 10°C/min, second heat): T_g 84°C, T_m (onset) 114°C, T_m (peak) 241°C, T_m (end) 324°C, H_f 29 J/g.

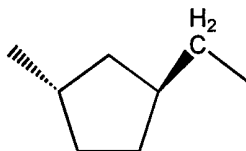
Example 32

Inside a dry box, a sample of [(2,6-iPrMePhN)₂NB]NiBr₂ from Example 28 (0.054 g, 0.089 mmol) was charged to a glass bottle. A 60 mL portion of a solution of cyclopentene (80 mL, 10,000 equivalents/Ni) in 120 mL 1,2,4-trichlorobenzene was added to the bottle. The polymerization was initiated with stirring by first adding tris(pentafluorophenyl)borane (0.28 g, 6 equivalents/Ni) followed by a 1.9 M solution of triethylaluminum in toluene (0.30 mL, 6 equivalents/Ni). After 30 min, the solution was diluted with the remaining cyclopentene solution. After 7 days, the dark brown solution would gel upon standing. After 14 days, the polymer was dispersed in a blender with 250 mL toluene and 8-hydroxyquinoline (0.42 g, 0.39 mmol). The yellow-green catalyst residues were extracted by diluting with 250 mL methanol. The polymer was filtered off and washed with methanol three times until the filtrate was colorless, then treated with a 0.5% solution of Irganox[®] 1010 in acetone. The polymer was dried at 120°C in a nitrogen-purged vacuum oven to give 41.64 g (6800 turnovers/Ni) polycyclopentene. DSC (0-350 °C, 10°C/min, second heat): T_g 100°C, T_m (onset) 117 °C, T_m (peak) 255°C, T_m (end) 328°C, H_f 38 J/g.

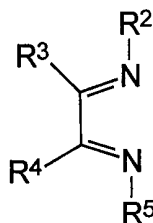
CLAIMS

What is claimed is:

1. A polymer, comprising, repeat units derived from one or more of 3-methylcyclopentene, 4-methylcyclopentene, 3-ethylcyclopentene or 3-cyclopentylcyclopentene, and optionally cyclopentene, provided that when said polymer is a homopolymer of 3-methylcyclopentene, at least about 40 mole percent of repeat units present are of the formula



2. A process for the polymerization of one or more olefins selected from the group consisting of 3-methylcyclopentene, 4-methylcyclopentene, 3-ethylcyclopentene and 3-cyclopentylcyclopentene, and optionally cyclopentene, by containing, at a temperature of -100°C to about $+200^{\circ}\text{C}$, said olefin with an olefin polymerization catalysts system containing a nickel or palladium complex of a compound of the formula
- 20

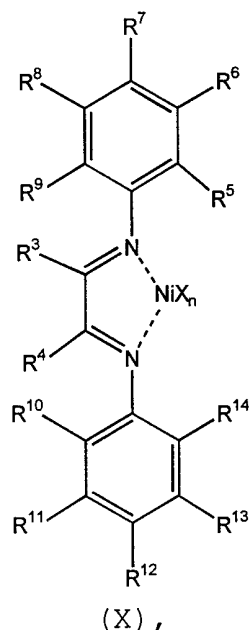


and optionally other cocatalysts, wherein

- R^2 and R^5 are each independently hydrocarbyl or substituted hydrocarbyl, provided that the carbon atom bound to the imino nitrogen atom has at least two carbon atoms bound to it; and
- 25

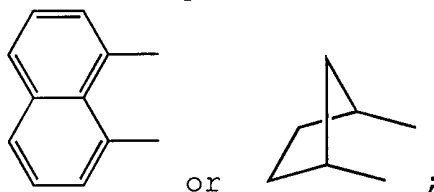
- R^3 and R^4 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or R^3 and R^4 taken together are hydrocarbylene or substituted hydrocarbylene to form a carbocyclic ring.
- 30

3. A compound of the formula



wherein:

- 5 each X is independently an anion;
 n is 2 or 3;
 R³ and R⁴ taken together are

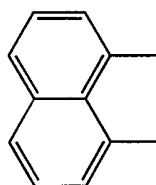


- R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, and R¹⁴ are
 10 each independently hydrogen, hydrocarbyl, substituted
 hydrocarbyl or a functional group;

 and provided that:

- when R⁵ is the same as R¹⁰, and R⁹ is the same
 as R¹⁴, said compound is in an anti form;
 15 no more than one of R⁵, R⁹, R¹⁰, and R¹⁴ is
 hydrogen;
 any two of R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³,
 and R¹⁴ vicinal to one another may form a ring; and
 R⁵ is different than R⁹.

- 20 4. The compound as recited in claim 3 wherein R³
 and R⁴ taken together are



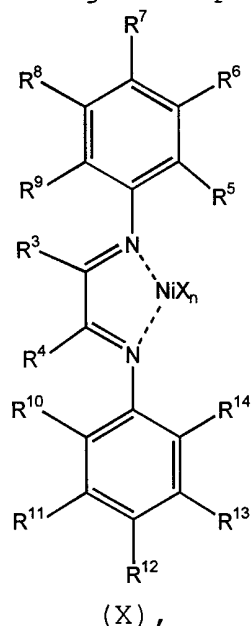
5. The compound as recited in claim 4 wherein R^5 , R^9 , R^{10} , and R^{14} are all alkyl.

no more than one of R^5 , R^9 , R^{10} , and R^{14} is
5 hydrogen;

6. The compound as recited in claim 4 wherein R^5 and R^{10} are methyl, and R^9 and R^{14} are identical alkyl groups having 2 or more carbons.

7. The compound as recited in claim 6 wherein R^9
10 and R^{14} are isopropyl.

8. A process for the polymerization of one or more
of cyclopentene and a substituted cyclopentene,
comprising, contacting, at a temperature of -100°C to
about $+200^\circ\text{C}$, said olefin with a olefin polymerization
15 catalyst system containing a compound of the formula

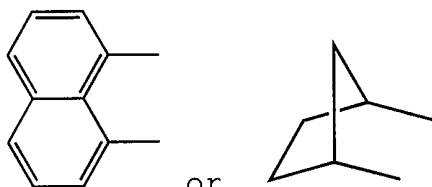


and optionally cocatalysts, wherein:

each X is independently a monoanion;

20 n is 2 or 3;

R^3 and R^4 taken together are



or ;

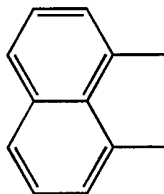
$R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13},$ and R^{14} are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl or a functional group;

5 and provided that:

when R^5 is the same as R^{10} , and R^9 is the same as R^{14} , said compound is in an anti form;

any two of $R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13},$ and R^{14} vicinal to one another may form a ring; and
 10 R^5 is different than R^9 .

9. The process as recited in claim 8 wherein R^3 and R^4 taken together are



10. The process as recited in claim 9 wherein $R^5,$
 15 $R^9, R^{10},$ and R^{14} are all alkyl.

11. The process as recited in claim 9 wherein R^5 and R^{10} are methyl, and R^9 and R^{14} are identical alkyl groups having 2 or more carbons.

12. The process as recited in claim 11 wherein R^9
 20 and R^{14} are isopropyl.

13. A homopolycyclopentene that has an end of melting point of 325°C to about 380°C .

14. The homopolycyclopentene as recited in claim 13 wherein said end of melting point is about 340°C to
 25 about 380°C .