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(54) Title: PROCESS USING BORANE DERIVED CATALYSTS FOR PREPARATION OF SYNDIOTACTIC VINYL AROMATIC POLYMERS

(57) Abstract

A process for preparing syndiotactic vinyl aromatic polymers comprising contacting at least one polymerizable vinyl aromatic monomer under polymerization conditions with a catalyst comprising a compound corresponding to the formula: $L_mMX_n + RA$, wherein L is a delocalized π-bonding group containing up to 50 nonhydrogen atoms; m is 0 or 1; M is a metal of Group 4 of the Periodic Table; X each occurrence is an inert, anionic ligand containing up to 20 nonhydrogen atoms; n is an integer greater than or equal to 1 and the sum of m and n is one less than the valence of M; and RA is $RB(C_6F_5)C_3$, where R is hydride, hydrocarbyl, silyl, a combination thereof or a substituted derivative thereof having up to 20 nonhydrogen atoms. Also included is a process for preparing the catalyst.

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PROCESS USING BORANE DERIVED CATALYSTS FOR PREPARATION OF SYNDIOTACTIC VINYL AROMATIC POLYMERS

The present invention relates to a process for polymerizing vinyl aromatic monomers, such as styrene, to produce polymers having a high degree of syndiotacticity, and in particular to a process for preparing polymers of vinyl aromatic monomers having a high degree of syndiotacticity using an alkylalumoxane-free catalyst. More particularly still, this invention relates to such a process using catalyst compositions obtained by abstraction of a leaving group from inert Group 4 metal compounds with a borane. The resulting polymers may be usefully employed in the preparation of solid objects and articles such as a moldings, films, sheets and foamed objects by molding, casting or the like process.

In US-A-4,680,353 there is disclosed a process for the preparation of polymers of vinyl aromatic monomers having a stereoregular structure of high syndiotacticity by the use of certain coordination catalysts. Particularly disclosed were the reaction products of a titanium compound and an organoaluminum compound, especially polymethylaluminoxane. The process disclosed in this patent requires the use of large amounts of the polymethylaluminoxane which is very expensive and difficult to make due to its very complex structure. Also, this process requires an expensive polymer purification system to remove remaining catalyst components due to the use of large amounts of the polymethylaluminoxane.

In EP-A-277,004 there are disclosed certain bis(cyclopentadienyl) metal compounds formed by reacting a bis(cyclopentadienyl) metal complex with salts of Bronsted acids containing a non-coordinating compatible anion. The reference discloses the fact that such complexes are usefully employed as catalysts in the polymerization of olefins.

In J. Am. Ch. Soc. 113, 3623-3625 (1991) there is disclosed a process for preparation of "cation like" zirconocene polymerization complexes by alkyl abstraction using tris(pentafluorophenyl)borane. The complexes were stated to have olefin polymerization activity roughly comparable to typical zirconocene/alumoxane complexes.

According to the present invention there is now provided a process for preparing polymers of vinyl aromatic monomers having a high degree of syndiotacticity which process comprises contacting at least one polymerizable vinyl aromatic monomer under polymerization conditions with a catalyst comprising a metal complex corresponding to the formula:

$L_mMX_n^- \ RBY_3^-$, wherein:

L is a delocalized π-bonding group or substituted group containing up to 50 nonhydrogen atoms;

m is 0 or 1;

M is a metal of Group 4 of the Periodic Table;

X each occurrence is an inert, anionic ligand containing up to 20 nonhydrogen atoms;

n is an integer greater than or equal to 1 and the sum of m and n is one less than the valence of M;

R is hydrocarbyl, silyl, a combination thereof or a substituted derivative thereof having up to 20 nonhydrogen atoms;

B is boron; and

Y is an inert covalently bound group having up to 40 atoms and BY_3 is a stable borane compound able to abstract an R group from a compound of the formula L_mMX_nR.

The preceding formula is referred to as the limiting, charge separated structure. However, it is to be understood that, particularly in solid form, the catalyst may not be fully charge separated. That is, the R group may retain a partial covalent bond to the metal atom, M. Thus, the catalysts may be alternately depicted as possessing the formula:

$$L_mMX_r \cdot\cdot R \cdot\cdot BY_3.$$

The catalysts are prepared by contacting a Group 4 metal containing compound of the formula:

$$L_mMX_nR$$

with the borane compound in an inert diluent. Alternatively, the catalysts may be prepared by contacting a Group 4 metal containing compound that is devoid of R groups with the borane compound in the presence of an aluminum compound of the formula AlR_3. Stated more explicitly the steps of this process comprise contacting a Group 4 metal containing compound of the formula:

$$L_mMX_{n+1}$$

with a borane compound of the formula BY_3 in the presence of an aluminum compound of the formula AlR_3 in an inert diluent under conditions to cause abstraction of at least one R group from the aluminum compound and assimilation thereof in the resulting borane containing complex.

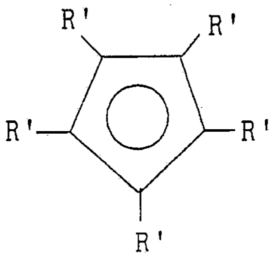
As used herein, the term "syndiotactic" refers to polymers having a stereoregular structure of greater than 50 percent syndiotactic of a racemic triad as determined by C^{13} nuclear magnetic resonance spectroscopy. Such polymers may be usefully employed in the preparation of articles and objects (for example, via compression molding, injection molding or other suitable technique) having an extremely high resistance to deformation due to the effects of temperature.

The term "substituted" when used with reference to L or R means inert substituent groups, including such groups as aralkyl, alkaryl, haloalkyl, silylalkyl, haloalkyl, haloaryl, haloalkaryl, halosilyl, haloalkarylsilyl, alkoxyalkyl, and so forth.

The term "inert" means noninterfering with the desired catalyst preparation or with the use of the resulting metal complex containing compound as a polymerization catalyst.

All reference to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 1989. Also, any reference to a Group or Series shall be to the Group or Series as reflected in this Periodic Table of the Elements, utilizing the IUPAC system for numbering groups.

Preferred compositions according to the present invention are those wherein m is 1, n is 2, and L is a cyclopentadienyl or substituted cyclopentadienyl group. Examples of cyclopentadienyl and substituted cyclopentadienyl groups for use according to the present invention are groups depicted by the formula:



wherein:

R' each occurrence is independently selected from the group consisting of hydrogen, halogen, R, N-R_2, P-R_2; OR; SR or BR_2, wherein R is as previously defined. Preferably, R' is alkyl or haloalkyl of up to 6 carbons. Preferred delocalized π-bonding groups are cyclopentadiene and substituted cyclopentadiene, especially pentamethylcyclopentadiene.

Most preferably M is titanium.

Illustrative but nonlimiting examples of X include R, halo, NR_2, PR_2, OR, SR, BR_2, etc. Preferably X each occurrence is R, NR_2 or OR.

Illustrative, but not limiting examples of suitable metal derivative compounds include: tetranorborene titanium, tetrabenzyl zirconium, tetraneopentyl titanium, (cyclopentadienyl)dimethyl(isopropoxy)titanium, (cyclopentadienyl)dibenzyl-(isopropoxy)titanium, (cyclopentadienyl)dibenzyl(phenoxy)zirconium, (cyclopentadienyl)dibenzyl(isopropoxy)hafnium, (cyclopentadienyl)dimethylzirconium chloride, bis(phenoxy)di(trimethylsilyl)zirconium, phenoxytrimethylzirconium, bis(2,6-diisopropyl-4-methyl)phenoxy)dibenzyltitanium, bis(2,4,6-trimethylphenoxy)dibenzyltitanium, tri(tertiarybutyl)siloxytrimethyl zirconium, bismethoxydi(phenylmethyl)titanium, bis(2,4,6-trimethylphenoxy)dibenzyltitanium, triphenoxybenzyltitanium, butoxytris((trimethylsilyl)methyl)zirconium, dimethoxydimethylzirconium, 4-(1-methyl-1-(4-methoxyphenyl)ethyl)phenoxy tribenzyl titanium, dinorborene dichlorotitanium, tribenzyltitanium hydride, cyclopentadienyltribenzylzirconium, cyclopentadienyltribenzyltitanium, cyclopentadienyltrimethyltitanium, cyclopentadienyltrimethylzirconium, cyclopentadienyltrineopentyltitanium, cyclopentadienyltri(diphenylmethyl)zirconium, cyclopentadienyltriphenylzirconium, cyclopentadienyltrineopentylzirconium, cyclopentadienyltri(m-tolyl)zirconium, cyclopentadienyltri(p-tolyl)zirconium, cyclopentadienyldimethyltitanium hydride, cyclopentadienyltri(diphenylmethyl)zirconium, pentamethylcyclopentadienyltrimethylzirconium, ethylcyclopentadienyltrimethylzirconium, pentamethylcyclopentadienyltribenzylzirconium, n-butylcyclopentadienyltrineopentyltitanium, (t-butylcyclopentadienyl)tri(trimethylsilyl)zirconium, cyclohexylcyclopentadienyltrimethylzirconium, (pentamethylcyclopentadienyl)dimethylzirconium chloride, indenyldibenzyltitanium chloride, (pentamethylcyclopentadienyl)diisopropoxy hafnium chloride, (benzylcyclopentadienyl)di(m-tolyl) titanium chloride, (diphenylcyclopentadienyl)dinorborneylzirconium chloride, pentamethylcyclopentadienyltriphenylzirconium, tetraethylcyclopentadienyltribenzylzirconium, propylcyclopentadienyltrimethylzirconium, propylcyclopentadienyltrimethylzirconium, (n-butylcyclopentadienyl)dimethyl(n-butoxy)titanium, cyclopentadienyldiphenylisopropoxyzirconium, cyclohexylmethylcyclopentadienyltribenzylzirconium, cyclohexylmethylcyclopentadienyltrimethylzirconium, cyclopentadienylmethylzirconium dihydride, benzylcyclopentadienyltrimethylhafnium, indenyltribenzylzirconium, trimethylsilylcyclopentadienyltrimethylzirconium, trimethylgermylcyclopentadienyl)trimethyltitanium, trimethylstannylcyclopentadienyltribenzylzirconium, (pentatrimethylsilyl)cyclopentadienyltrimethylzirconium, trimethylsilylcyclopentadienyltrimethylzirconium, penta(trimethylsilyl)cyclopentadienyltribenzyltitanium, trimethylgermylcyclopentadienyltriphenylhafnium, trifluoromethylcyclopentadienyltrimethylzirconium, trifluoromethylcyclopentadienyltrinorborneylzirconium, trifluoromethylcyclopentadienyltribenzylzirconium, cyclopentadienyltrimethylsilylzirconium, cyclopentadienyltri(phenyldimethylsilyl)zirconium, and the like.

Other compounds which are useful in the catalyst compositions of this invention will, of course, be apparent to those skilled in the art.

Suitable borane compounds for use herein particularly include tris(fluoroaryl) and tris (trifluoromethyl substituted aryl) borane compounds, or other suitable inertly substituted borane compounds. Examples include tris(pentafluorophenyl)borane, tris(2,3,5,6-tetrafluorophenyl)borane, tris(3,5-di(trifluoromethyl)phenyl)borane, etc. Especially preferred are perfluorinated compounds such as tris(pentafluorophenyl)borane.

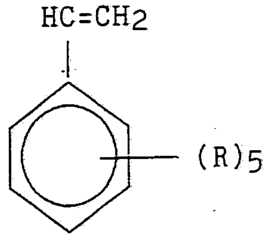
In general, the catalyst can be prepared by combining the metal compound and borane compound (or by combining the metal compound, borane compound and AlR_3) in a suitable solvent at a temperature within the range from -100°C to 100°C, preferably 0 to 50°C. The presence of residual aluminum containing species in the catalyst system is not detrimental to catalyst performance. The catalyst system can also form *in situ* if the components thereof are added directly to the polymerization process and a suitable solvent or diluent, including condensed monomer, is used in said polymerization process. It is, however, preferred to form the catalyst in a separate step in a suitable solvent prior to adding the same to the polymerization step. The catalysts' components are generally sensitive to both moisture and oxygen and should be handled and transferred in an inert atmosphere such as nitrogen, argon or helium.

When the catalysts of the invention are prepared by combining the metal compound, borane compound and AlR_3 it is believed that a transfer of one or more R groups to the metal compound first occurs. Upon interacting with the borane compound, one of the R groups is then abstracted by the borane to form the ultimate catalytic species. Thus by this technique the metal compound initially utilized may be a metal alkoxide or similar compound which by itself would not be suitable for use in combination with the borane.

As previously indicated, the improved catalyst of the present invention will, preferably, be prepared in a suitable solvent or diluent. Suitable solvents or diluents include any of the solvents known in the prior art including, but not necessarily limited to, straight and branched-chain hydrocarbons such as C_{6-12} alkanes (hexane, heptane and octane); C_{6-12} cyclic and alicyclic, aliphatic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, and methylcycloheptane; C_{6-12} aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and decalin; and mixtures thereof.

In general, catalysts according to the present invention can be selected so as to produce polymer products that will be free of certain trace metals generally found in polymers produced with Ziegler-Natta type catalysts containing cocatalysts such as aluminum or magnesium based compounds.

In the practice of the present invention, vinyl aromatic monomers can be polymerized in the presence of the catalyst as mentioned above. Suitable vinyl aromatic monomers which can be polymerized in the process of the present invention include those represented by the formula:



wherein each R is independently hydrogen; an aliphatic, cycloaliphatic or aromatic hydrocarbon group having from 1 to 10, more suitably from 1 to 6, most suitably from 1 to 4, carbon atoms; or a halogen atom. Examples of such monomers include, styrene, chlorostyrene, n-butyl styrene, p-vinyl toluene etc. with styrene being especially suitable. Copolymers of styrene and the above vinyl aromatic monomers other than styrene can also be prepared.

The polymerization may be conducted under slurry, bulk or suspension polymerization conditions or other suitable reaction conditions including solid, powdered reaction conditions. The polymerization can be conducted at temperatures of from 0°C to 160°C, preferably from 25°C to 100°C, more preferably from 30°C to 80°C, for a time sufficient to produce the desired polymer. Typical reaction times are from one minute to 100 hours, preferably from 1 to 10 hours. The optimum reaction time or reactor residence time will vary depending upon the temperature, solvent and other reaction conditions employed. The polymerization can be conducted at subatmospheric pressure as well as superatmospheric pressure, suitably at a pressure within the range of 1 to 500 psig (6.9 kPa-3,400 kPa). The use of ambient or low pressures, for example, 1-5 psig (6.9-34.5 kPa) is preferred in view of lower capital and equipment costs.

The polymerization may be conducted in the presence of an inert diluent or solvent or in the absence thereof. In the latter event excess monomer serves as a diluent. Examples of suitable, nonreactive diluents or solvents include C_{6-20} aliphatic, cycloaliphatic, aromatic and halogenated aliphatic or aromatic hydrocarbons, as well as mixtures thereof. Preferred nonreactive diluents comprise the C_{6-10} alkanes, toluene and mixtures thereof. A particularly desirable diluent for the polymerization is iso-octane, iso-nonane or blends thereof such as Isopar-E®, available from Exxon Chemical Company. Suitable amounts of solvent are employed to provide a monomer concentration from 5 percent to 100 percent by weight.

The molar ratio of the vinyl aromatic monomer to the catalyst (in terms of metal) may range from 100:1 to 1,000,000:1, preferably from 3,500:1 to 200,000:1. In the case of using a solvent, the catalyst may be used at a concentration with the range from 10^{-7} to 10^{-1} moles per liter of solvent.

As in other similar polymerizations it is highly desirable that the monomers and solvents employed be of sufficiently high purity that catalyst deactivation does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressures, contacting with molecular sieves or high surface area alumina, deaeration, etc. may be employed. In addition a small amount of an aluminum trialkyl compound or similar scavenger may be added to the reaction mixture to protect the catalyst from deactivation by contaminants in the reaction mixture.

Purification of the resulting polymer to remove entrained catalyst may also be desired by the practitioner. Purification of the resulting polymer prepared by the process of this invention is much easier than purification of polymer prepared by a conventional process since the process of this invention does not use polyalkylaluminoxane,which is used in large quantities as cocatalyst in conventional processes. Entrained catalyst may generally be identified by residues of ash on pyrolysis of the polymer that are attributable to catalyst metal values. A suitable technique for removing such compounds is by solvent extraction, for example, extraction utilizing hot, high boiling chlorinated solvents, acids or bases, such as caustic, followed by filtration. However, because of the small amounts of catalyst used in the process, polymer purification is normally not necessary.

Having described the invention, the following examples are provided as further illustrative and are not to be construed as limiting. Unless stated to the contrary, all parts and percentages are based on weight.

Example 1

Preparation of Catalyst

A dry 2 ml volumetric flask was charged with 0.70 ml of a 0.0069M toluene solution of pentamethylcyclopentadienyltitanium tribenzyl under an argon atmosphere Next, 97 µl of a 0.05M solution of tri(pentafluorophenyl) boron in toluene was added. Additional toluene was added to fill the flask. The contents were stirred for one hour at 25°C resulting in the formation of a 0.00241M solution of a composition having a charge separated, limiting structure corresponding to the formula:

$$[CpTiBz]^{+}\ [BzB(C_6F_5)_3]^{-}$$

wherein Cp is cyclopentadienyl and Bz is benzyl.

Preparation of Syndiotactic Polystyrene

A dry 20 ml vial was charged with 10.0 ml (87.4 mmol) of purified styrene and 20µl of a 1M solution of triisobutyl aluminum in toluene. The vial was capped with a teflon coated septa and a metal crimp cap, and placed in a water bath at 70°C. After 10 minutes 250µl of the above catalyst composition was added, giving a total molar ratio of styrene:Ti:borane:triisobutyl aluminum of 145,000:1:1:33. After 1 hour the vial was removed from the water bath and the polymerization was stopped by the addition of 2ml of methanol. The off-white, insoluble product was washed with methanol and dried in-vacuo to obtain 5.2 gm of a resultant polymer. The polymer was insoluble in methylene chloride or other common solvents for atactic polystyrene, and had a melting point of 270.4°C (by DSC), consistent with polystyrene having a syndiotacticity of greater than 98 percent. Yield was 0.45 g, 5.0 percent. Molecular weight (Mw) determined by viscosity comparison of o-dichlorobenzene solutions of samples of known molecular weight was 221,000.

Example 2

The reaction conditions of Example 2 were repeated excepting that the titanium compound used was pentamethylcyclopentadienyltrismethoxy titanium (4.8 µmol) and 26.5 µl of a 1M toluene solution of triisobutyl aluminum was added to the titanium compound before addition of the borane solution. The mixture of titanium compound, triisobutyl aluminum and tri(pentafluorophenyl)borane was allowed to interact while being stirred for 1.5 hours. The resulting catalyst solution was a medium brown color. The polymerization conditions of Example 1 were substantially repeated. The resulting polymer had a crystalline melting point of 270.2°C, consistent with a polymer having greater than 98 percent syndiotacticity. Yield was 11.5 percent. Mw as determined by viscosity comparison techniques was 814,000.

Comparative

When the above reaction conditions were repeated without addition of the triisobutyl aluminum solution, no polymerization occurred.

Example 3

The reaction conditions of Example 2 were substantially repeated excepting that 48 µl of a 1M toluene solution of triisobutyl aluminum was added to the pentamethylcyclopentadienyltrismethoxy titanium compound before addition of the borane solution. In addition 1.25 ml of the 0.05M solution of tri(pentafluorophenyl) borane was used. The mixture of titanium compound, triisobutyl aluminum and tri(pentafluorophenyl)borane was allowed to interact while being stirred for 1.5 hours. The resulting catalyst solution was a medium brown color. The polymerization conditions of Example 3 were also repeated The final molar ratio of styrene: Ti:borane:triisobutyl aluminum was 145,000:1:13:43. The resulting polymer had a crystalline melting point of 269.6°C, consistent with a polymer having greater than 98 percent syndiotacticity. Yield was 8.3 percent. Mw was 763,000.

Claims :

1. A process for preparing polymers of vinyl aromatic monomers having a high degree of syndiotacticity comprising contacting at least one polymerizable vinyl aromatic monomer at a temperature from 0 to 160°C and a pressure from 110 KPa to 3.5 MPa with a catalyst comprising a metal complex corresponding to the formula:

$L_mMX_n + RBY_3^-$, wherein:

L is a delocalized π-bonding group or substituted group containing up to 50 nonhydrogen atoms;

m is 0 or 1;

M is a metal of Group 4 of the Periodic Table;

X each occurrence is an inert, anionic ligand containing up to 20 nonhydrogen atoms;

n is an integer greater than or equal to 1 and the sum of m and n is one less than the valence of M;

R is hydrocarbyl, silyl, a combination thereof or a substituted derivative thereof having up to 20 nonhydrogen atoms;

B is boron; and

Y is an inert covalently bound group having up to 40 atoms and BY_3 is a stable borane compound able to abstract an R group from a compound of the formula L_mMX_nR

2. The process according to Claim 1 wherein the monomer is contacted with the catalyst in the presence of a solvent selected from the group consisting of C_{6-20} aliphatic, cycloaliphatic, aromatic, halogenated aliphatic, halogenated aromatic hydrocarbons and mixtures thereof.

3. The process according to Claim 1, wherein the molar ratio of the vinyl aromatic monomer to the catalyst ranges from 100:1 to 1,000,000:1.

4. The process according to Claim 1 wherein the vinyl aromatic monomer is styrene.

5. The process according to Claim 1 wherein M is titanium.

6. The process according to Claim 1 wherein L is cyclopentadiene or pentamethylcyclopentadiene.

7. The process according to Claim 1 wherein X each occurrence is R, NR_2 or OR

8. A process for preparing a composition corresponding to the formula:

$L_mMX_n^+ \; RBY_3^-$, wherein:

L is a delocalized π-bonding group or substituted group containing up to 50 nonhydrogen atoms;

m is 0 or 1;

M is a metal of Group 4 of the Periodic Table;

X each occurrence is an inert, anionic ligand containing up to 20 nonhydrogen atoms;

n is an integer greater than or equal to 1 and the sum of m and n is one less than the valence of M;

R is hydrocarbyl, silyl, a combination thereof or a substituted derivative thereof having up to 20 nonhydrogen atoms;

B is boron; and

Y is an inert covalently bound group having up to 40 atoms and BY_3 is a stable borane compound able to abstract an R group from a compound of the formula L_mMX_nR, the steps of the process comprising contacting a Group 4 metal containing compound of the formula:

L_mMX_{n+1}.

with a borane compound of the formula BY_3 in the presence of an aluminum compound of the formula AlR_3 in an inert diluent at a temperature from -100°C to 100°C to cause abstraction of at least one R group from the aluminum compound and assimilation thereof in the resulting borane containing complex.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/05823

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :CO8F 4/64, 4/643, 2/06.
US CL :526/131
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)

U.S. : 526/131, 526/134, 346, 347.2

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 practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,Y	US, A, 5,064,802 (STEVENS et al) 12 NOVEMBER 1991 see column 6, lines 55 to 68; column 7, lines 20-28 and 61-68; and column 8, lines 41-44.	1-7
P,Y	US, A, 5,066,741 (CAMPBELL, JR.) 19 NOVEMBER 1991 column 7, line 56 to column 8, line 16; column 9, lines 50-53 and Examples 17-22.	1-7
Y	WO, A, WO 91/09882 (EXXON CHEMICAL PATENTS, INC.) 11 JULY 1991 see page 18, lines 21-22 and page 24, lines 27-30.	1-7
Y	EP, A, 0 277 004 (EXXON CHEMICAL PATENTS, INC.) 03 AUGUST 1988 see page 8, line 63 to page 9, line 10 and page 10, lines 7-10.	1-7

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search
03 DECEMBER 1992

Date of mailing of the international search report
05 JAN 1993

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INTERNATIONAL SEARCH REPORT	International application No. PCT/US92/05823

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
Please See Extra Sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any addtional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention frist mentioned in the claims; it is covered by claims Nos.:
1-7

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

Group I, claims 1-7, drawn to a process for preparing polymers of vinyl aromatic monomers, classified in class 526, subclass 131.

Group II, claim 8, drawn to a process for preparing a composition, classified in class 568, subclass 1+.

The groups of inventions are not so linked as to form a single inventive concept. In particular, this application contains a claim only to a process for preparing a catalyst composition and claims to the use of said composition, with no composition claim being present. There is lack of unity of invention since the provisions of PCT Rule 13.2 (i) do not apply, and since the process for preparing the composition is independent of the use of the composition since neither is dependent on the other.