

APPLICATION ACCEPTED AND AMENDMENTS

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COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

CONVENTION APPLICATION FOR A STANDARD PATENT

70492/87

We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., of Carel van Bylandtlaan 30, 2596 HR The Hague, the Netherlands hereby apply for the grant of a standard patent for an invention entitled: "~~POLYMER PREPARATION~~" "PROCESS FOR THE PREPARATION OF POLYMERS OF CARBON MONOXIDE AND ETHENE" which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION

Number of Basic Application:-
8600744

Name of Convention Country in which Basic Application was filed:-
the Netherlands

Date of Basic application:-
24 March, 1986

Our address for service is:-

C/- Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTIETH day of MARCH 1987

SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

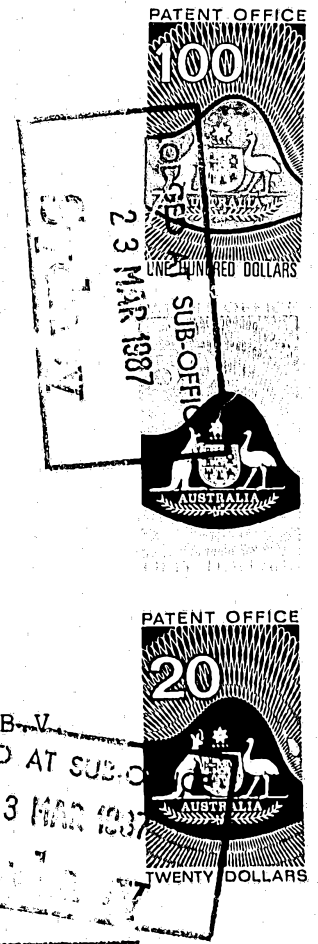
By:

M.J. Anderson
Registered Patent Attorney.

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COMMONWEALTH OF AUSTRALIA

Patents Act 1952-55

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION
FOR A PATENT

In support of the Convention Application made by
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
for a patent for an invention entitled:

"Polymer preparation"

I, Onno Aalbers, of Carel van Bylandtlaan 30, The Hague,
the Netherlands, do solemnly and sincerely declare as follows:

1. I am authorized by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.,
the applicant for the patent, to make this declaration on its
behalf.
2. The basic application~~(*)~~ as defined by Section 141 of the Act
was~~xxxx~~made in the Netherlands
on the 24th day of March, 1986
by SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
3. Joannes Adrianus Maria VAN BROEKHOVEN, a Netherlands national
and Michael John DOYLE, a British national, both of Badhuisweg 3,
1031 CM Amsterdam, the Netherlands

~~xx~~/are the actual inventor(s) of the invention and the facts upon
which the Applicant Company is entitled to make application are as
follows: as Assignees of the inventor(s).

4. The basic application~~xx~~ referred to in paragraph 2 of this
Declaration was~~xxxx~~ the first application~~(*)~~ made in a Convention
Country in respect of the invention the subject of the application.

Declared at Dated this 27 day of February, 1987
The Hague

Signature of Declarant

To: The Commissioner of Patents,
Commonwealth of Australia

JB2H04



COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

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This document contains the
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printing.

Name of Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ
B.V.

Address of Applicant: Carel van Bylandtlaan 30, 2596 HR The
Hague, the Netherlands

Actual Inventor(s): JOAHNNES ADRIANUS MARIA VAN BROEKHOVEN and
MICHAEL JOHN DOYLE

Address for Service: Spruson & Ferguson, Patent Attorneys,
Level 33 St Martins Tower, 31 Market
Street, Sydney,
New South Wales, 2000, Australia

Complete Specification for the invention entitled:

"PROCESS FOR THE PREPARATION OF POLYMERS OF CARBON
~~"POLYMER PREPARATION"~~
MONOXIDE AND ETHENE"

The following statement is a full description of this invention,
including the best method of performing it known to us

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~~POLYMER PREPARATION~~
PROCESS FOR THE PREPARATION OF POLYMERS OF
CARBON MONOXIDE AND ETHENE

The invention relates to a process for the preparation of polymers of carbon monoxide and ethene.

High molecular weight linear polymers of carbon monoxide and ethene in which the monomer units occur in an alternating order and therefore consist of units of the formula $-\text{CO}-(\text{C}_2\text{H}_4)-$, can be prepared by using catalyst compositions based upon

- a) a palladium compound,
- b) an anion of an acid with a pKa of less than 2, provided that the acid is not a hydrohalogenic acid, and
- c) a bidentate ligand of the general formula $\text{R}^1\text{R}^2-\text{M}-\text{R}-\text{M}-\text{R}^3\text{R}^4$ wherein M represents phosphorus, arsenic or antimony, R^1 , R^2 , R^3 and R^4 represent hydrocarbyl groups which may or may not be substituted with polar groups and R represents a bivalent organic bridging group which contains at least two carbon atoms in the bridge.

In the above-mentioned polymer preparation both reaction rates and molecular weights of the polymers obtained play a major role. On the one hand the highest possible reaction rate should be aimed at in the polymer preparation, while on the other hand the polymers are more valuable with a view to their uses according as they have higher molecular weights. Both reaction rates and molecular weights can be influenced by the temperatures and overall pressures applied during the polymerization. Higher reaction rates and lower molecular weights will be obtained according as higher reaction temperatures are chosen. Higher reaction rates and higher molecular weights will be obtained according as higher overall pressures are chosen. The effect which a rise in reaction temperature and overall pressure has on reaction rates is greatest at reaction temperatures below 85 °C and overall pressures below 75 bar. Above these values increased reaction temperatures and overall pressures will still



lead to higher reaction rates but the increase will become increasingly smaller. In view of the above, the polymers used to be hitherto prepared mainly at a reaction temperature in the range of from 60 to 70 °C and at an overall pressure in the range of from 50 to 60 bar. A correct choice of reaction temperatures and overall pressures within the said ranges allowed polymers of sufficiently high molecular weights for the relevant application to be produced at acceptable reaction rates. Attempts to achieve an increase in reaction rate by varying the ratio between the ethene partial pressure and the carbon monoxide partial pressure remained unsuccessful. It was found that at overall pressures below 75 bar variations in the ratios between ethene partial pressure and carbon monoxide partial pressure ranging from 0.3 to 3 did not lead to any significant change in the reaction rate. Neither were variations of the partial pressure ratios within the same range seen to have any significant influence on the molecular weights of the polymers obtained.

The Applicant has carried out an investigation into the execution of the polymerization at overall pressures between 75 and 250 bar while using ethene/carbon monoxide partial pressure ratios between 0.3 and 3. As could be expected from the results of low pressure polymerization found earlier, variation of the ethene/carbon monoxide partial pressure ratio within a given high overall pressure proved to produce no significant change in the reaction rate. Surprisingly and in sharp contrast with the expectations based on earlier results of low pressure polymerization it has now been found that variation of the ethene/carbon monoxide partial pressure ratio at a given high overall pressure has a substantial effect on the molecular weights of the polymers obtained, in that polymers of considerably higher molecular weights are obtained when the polymerization is carried out at an ethene/carbon monoxide partial pressure ratio between 0.75 and 3 as opposed to polymers prepared at the same temperature and overall pressure but at an ethene/carbon monoxide partial pressure ratio between 0.3 and 0.75. The present find is of interest not only for the preparation of

5 polymers with higher molecular weights but also for the execution of the polymerization at increased reaction rates. For it is possible by increasing the ethene/carbon monoxide partial pressure ratio and simultaneously raising the reaction temperature to realise considerably higher reaction rates while the molecular weights of the polymers remain unchanged.

10 The present patent application therefore relates to a process for the preparation of polymers in which a mixture of carbon monoxide and ethene is polymerized at an overall pressure in the range of from 75 to 250 bar and an ethene/carbon monoxide partial pressure ratio in the range of from 0.75 to 3 by using a catalyst composition based upon

- 15 a) a palladium compound,
- b) an anion of an acid with a pKa lower than 2, provided that the acid is not a hydrohalogenic acid, and
- c) a bidentate ligand of the general formula $R^1R^2-M-R-M^3R^4$ wherein M represents phosphorus, arsenic or antimony, R^1 , R^2 , R^3 and R^4 represent hydrocarbyl groups which may or may not be substituted with polar groups and R represents a bivalent organic bridging group containing at least two carbon atoms in the bridge.
- 20

The patent application further relates to the polymers thus prepared and to shaped objects consisting at least partly of these polymers.

25 The process according to the invention is preferably carried out at an overall pressure between 80 and 200 bar and in particular between 85 and 175 bar. As regards the ethene/carbon monoxide partial pressure ratio used, preference is given to a ratio lying between 0.80 and 2.5 and in particular between 0.85 and 2. The polymerization is preferably carried out at a temperature between 30 20 and 200 °C and in particular between 30 and 150 °C. Furthermore, the polymerization is preferably carried out in a liquid diluent. Very suitable liquid diluents are lower alcohols such as methanol and ethanol. The quantity of catalyst composition used in the process according to the invention may vary within wide ranges. Per 35

mol of ethene to be polymerized such a quantity of catalyst composition is preferably used as to contain 10^{-7} - 10^{-3} and in particular 10^{-6} - 10^{-4} gram atom of palladium.

5 Preferably the palladium compound applied as component a) is a palladium salt of a carboxylic acid and in particular palladium acetate. Examples of suitable acids with a pKa lower than 2 (determined in aqueous solution at 18 °C) are sulphuric acid, perchloric acid, sulphonc acids, such as methanesulphonic acid, trifluoro-
10 methanesulphonic acid and para-toluenesulphonic acid and carboxylic acids such as trichloroacetic acid, difluoroacetic acid and trifluoroacetic acid. Preference is given to para-toluenesulphonic acid and trifluoroacetic acid.

In the catalyst compositions component b) is preferably present in a quantity of from 0.5 to 200 and in particular of from
15 1.0 to 100, equivalents per gram atom of palladium. Component b) may be introduced into the catalyst compositions either in the form of an acid or as a salt. Eligible salts are salts of non-noble transition metals and salts of main group metals. Examples of transition metals whose salts are very suitable for use as component
20 b) are the Group 4B metal zirconium, the Group 5B metal vanadium, the Group 6B metal chromium, the Group 8 metals iron and nickel, the Group 1B metal copper, the lanthanide cerium and the actinides thorium and uranium. If in the catalyst compositions component b) is used in the form of an acid or in the form of a
25 salt of a non-noble transition metal, it is preferred also to include a quinone as component d) in the catalyst compositions in order to enhance the activity of the latter. 1,4-Benzquinones have proved very useful for this purpose.

Examples of main group metals the salts of which can very
30 suitably be used as component b) are the Group 3A metals aluminium and gallium, the Group 4A metals tin and lead and the Group 5A metal antimony. Salts of Group 1A metals such as lithium, potassium and sodium and salts of Group 2A metals such as magnesium are also eligible for the purpose, provided that the catalyst compositions
35 also contain an ether as component d). It is preferred when a salt

of a metal belonging to the main groups 3A-5A is used as component b), that in addition an ether is included in the catalyst compositions as component d) in order to enhance their activity. Crown ethers have proved to be very suitable ethers.

5 Optionally the two components a) and b) can be combined and used in the form of a single compound. An example of such a compound is the complex $\text{Pd}(\text{CH}_3\text{CN})_2 (\text{O}_3\text{S}-\text{C}_6\text{H}_4-\text{CH}_3)_2$ which can be prepared by reacting a palladium chloride with the silver salt of para-toluenesulphonic acid in acetonitrile as the solvent.

10 In the bidentate ligand M is preferably phosphorus. The groups R^1 , R^2 , R^3 and R^4 present in the bidentate ligand preferably contain 6-14 carbon atoms. Special preference is given to bidentate ligands in which the groups R^1 , R^2 , R^3 and R^4 are phenyl groups or substituted phenyl groups. The bivalent organic bridging group R preferably contains three carbon atoms in the bridge. Examples of suitable bidentate ligands are

1,3-bis(di-p-tolylphosphino)propane,

1,3-bis[bis(p-methoxyphenyl)phosphino]propane,

1,3-bis(diphenylphosphino)propane, and

20 2-methyl-2-(diphenylphosphinomethyl)-1,3-bis(diphenylphosphine)propane.

Preferably either one of the latter two bidentate ligands is used. The bidentate ligand is preferably applied in a quantity of 0.1-5 and in particular 0.5-1.5 mol per mol of palladium compound.

25 The carbon monoxide used in the preparation of the polymers need not be pure. It may contain such contaminations as hydrogen, carbon dioxide and nitrogen.

30 The higher the molecular weight of the polymers according to the invention, the higher will be in general the intrinsic viscosity they exhibit. For the determination of the intrinsic viscosity of a polymer according to the invention, four solutions are first of all prepared by dissolving the polymer in four different concentrations at 100°C in m-cresol. For each of these solutions, the viscosity is measured in a viscometer at 100°C relative to m-cresol at 100°C. If T_0 represents the outflow time of m-cresol



and T_p the outflow time of the polymer solution, the relative viscosity (η_{rel}) is obtained from $\eta_{rel} = T_o/T_p$. From η_{rel} can be calculated the inherent viscosity (η_{inh}) according to the formula:

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

5 where c represents the concentration of the polymer in grams per 100 ml solution. By plotting graphically the η_{inh} found for each of the four polymer solutions against the corresponding concentration (c) and then by extrapolating to $c=0$, the intrinsic viscosity $[\eta]$ in dl/g is found. Instead of "intrinsic viscosity", this patent application will henceforth use the term
10 recommended by the International Union of Pure and Applied Chemistry, viz. "Limiting Viscosity Number" (LVN). The polymers according to the invention generally have an LVN of between 0.2 and 5.0 dl/g. Preferred polymers have an LVN of between 0.3 and 4.5 dl/g and in particular an LVN of between 0.4 and 4.0 dl/g.

15 The invention will now be illustrated with the aid of the following examples.

EXAMPLE 1

A carbon monoxide/ethene copolymer was prepared as follows.
20 200 ml of methanol was introduced into a mechanically stirred autoclave with a volume of 300 ml. After the contents of the autoclave had been brought to a temperature of 65 °C, ethene and CO were introduced in amounts equivalent to 18 bar and 36 bar, respectively. A catalyst solution was then introduced into the autoclave, consisting of:
25 18 ml of methanol,
0.03 mmol of palladium acetate,
0.03 mmol of 2-methyl-2-(methyldiphenylphosphine)-1,3-bis(diphenylphosphine)propane, and
0.06 mmol of p-toluenesulphonic acid.
30 The pressure was maintained at 55 bar by introduction under pressure of a 1:1 carbon monoxide/ethene mixture. After one hour the polymerization was terminated by releasing the pressure. The polymer was filtered off, washed with methanol and dried at 70 °C.

The product was 9.6 g of copolymer, so the polymerization rate was 3200 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 1.1 dl/g.

EXAMPLE 2

5 A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except that in this case ethene and CO were introduced into the autoclave both in amounts equivalent to 27 bar. The product was 10.5 g of copolymer, so the polymerization rate was 3500 g of copolymer/g of palladium/-
10 hour.

The copolymer had an LVN of 1.3 dl/g.

EXAMPLE 3

15 A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except for the following differences

a) ethene and CO were introduced into the autoclave in amounts equivalent to 5 bar and 10 bar, respectively,

b) the quantity of catalysts was 10/3 of the quantity used in Example 1,

20 c) the pressure was maintained at 16 bar by introduction of a 1:1 carbon monoxide/ethene mixture, and

d) the polymerization was terminated after 19 hours.

The product was 51 g of copolymer, so the polymerization rate was 270 g of copolymer/g of palladium/hour.

25 The copolymer had an LVN of 0.3 dl/g.

EXAMPLE 4

30 A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 3, except that in this case ethene and CO were introduced into the autoclave both in amounts equivalent to 7.5 bar. The product was 47 g of copolymer, so the polymerization rate was 250 g of copolymer/g of palladium/-hour.

The copolymer had an LVN of 0.4 dl/g.

EXAMPLE 5

A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except for the following differences

- 5 a) ethene and CO were introduced into the autoclave in amounts equivalent to 50 bar and 100 bar, respectively,
b) the quantity of catalyst was 5/3 of the quantity used in Example 1, and
c) the pressure was maintained at 151 bar by introduction of a 1:1
10 carbon monoxide/ethene mixture.

The product was 20 g of copolymer, so the polymerization rate was 4000 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 3.3 dl/g.

EXAMPLE 6

- 15 A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 5, except that in this case ethene and CO were introduced into the autoclave both in amounts equivalent to 75 bar. The product was 22 g of copolymer, so the polymerization rate was 4400 g of copolymer/g of palladium/hour.

20 The copolymer had an LVN of 5.1 dl/g.

EXAMPLE 7

A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 5, except for the following differences

- 25 a) the reaction temperature was 80 °C, and
b) the polymerization was terminated after 0.5 hour.

The product was 25 g of copolymer, so the polymerization rate was 10,000 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 1.1 dl/g.

30 EXAMPLE 8

A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 7, except that in this case ethene and CO were introduced into the autoclave both in amounts equivalent to 75 bar. The product was 25 g of copolymer, so

the polymerization rate was 10,000 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 2.4 dl/g.

EXAMPLE 9

5 A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except for the following differences

a) the reaction temperature was 35 °C,

b) the quantity of catalyst was 10/3 of the quantity used in
10 Example 1, and

c) the polymerization was terminated after 25 hours.

The product was 37 g of copolymer, so the polymerization rate was 150 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 5.3 dl/g.

15 EXAMPLE 10

A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except for the following differences

a) the reaction temperature was 40 °C, and

b) the polymerization was terminated after 20 hours.

The product was 18 g of copolymer, so the polymerization rate was 300 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 2.2 dl/g.

EXAMPLE 11

25 A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except that in this case the reaction temperature was 85 °C. The product was 15 g of copolymer, so the polymerization rate was 5000 g of copolymer/g of palladium/hour.

30 The copolymer had an LVN of 0.5 dl/g.

EXAMPLE 12

A carbon monoxide/ethene copolymer was prepared substantially in the same way as the copolymer of Example 1, except that in this case the reaction temperature was 110 °C. The product was 18 g of

copolymer, so the polymerization rate was 6000 g of copolymer/g of palladium/hour.

The copolymer had an LVN of 0.2 dl/g.

5 Of the Examples 1-12 only Examples 6 and 8 are examples according to the invention. In these examples the copolymers were prepared at an overall pressure of between 75 and 250 bar and an ethene/carbon monoxide partial pressure ratio of between 0.75 and 3. Examples 1-5, 7 and 9-12 fall outside the scope of the invention; they have been included in this patent application for
10 comparison.

With the aid of ^{13}C -NMR analysis it was established that the copolymers prepared according to Examples 1-12 had a linear alternating structure and therefore consisted of units of the formula $-\text{CO}-(\text{C}_2\text{H}_4)-$. All the copolymers prepared according to Examples 1-12
15 had a melting point of 257 °C.

Comparison of Examples 9, 10, 11 and 12, which were all carried out at the same overall pressure and ethene/carbon monoxide partial pressure ratio but at different reaction temperatures, shows that an increase in reaction temperature of from 35 to 100 °C
20 leads to an increased polymerization rate of from 150 to 6000 g of copolymer/g of palladium/hour, whereas the LVN drops from 5.3 to 0.2 dl/g. It is also seen that according as the temperatures used are higher, the positive influence this has on the polymerization rate decreases whilst the negative influence on the LVN is main-
25 tained.

Comparison of Examples 3, 1 and 5, which were all carried out at the same temperature and ethene/carbon monoxide partial pressure ratio but at different overall pressures, shows that an increase in the overall pressure of from 16 to 151 bar leads to an increased
30 polymerization rate of from 270 to 4000 g of copolymer/g of palladium/hour while at the same time the LVN increases from 0.3 to 3.3 dl/g.

Comparison of Example 1 with Example 2 and of Example 3 with Example 4, which were prepared in pairs at the same temperatures

and overall pressures but at different ethene/carbon monoxide partial pressure ratios, shows that an increase in partial pressure ratio from 0.5 to 1 at an overall pressure below 75 bar produces no significant change in either polymerization rate or LVN.

5 Comparison of Example 5 with Example 6 and of Example 7 with Example 8, which were carried out in pairs at the same temperatures and overall pressures but at different ethene/carbon monoxide partial pressure ratios, shows that an increase in partial pressure
10 produces no significant change in the polymerization rate, whereas the LVN increases considerably.

 Comparison of Example 6 with Example 9 and of Example 8 with Example 10, which produced pairs of copolymers having similar
15 the invention polymerization rates are achieved which are 29 and 33 times as high, respectively.

The claims defining the invention are as follows:

1. Process for the preparation of polymers characterized in that a mixture of carbon monoxide and ethene is polymerized at an overall pressure of between 75 and 250 bar and an ethene/carbon monoxide partial pressure ratio of between 0.75 and 3 by using a catalyst composition based upon

(a) a palladium compound,

(b) an anion of an acid with a pKa of less than 2, provided that the acid is not a hydrohalogenic acid, and

(c) a bidentate ligand of the general formula $R^1R^2-M-R-M^3R^4$, wherein M represents phosphorus, arsenic or antimony, R^1 , R^2 , R^3 and R^4 represent hydrocarbyl groups which may or may not be substituted with polar groups and R represents a bivalent organic bridging group which contains at least two carbon atoms in the bridge.

2. Process as claimed in claim 1, characterized in that it is carried out at an overall pressure of between 80 and 200 bar.

3. Process as claimed in claim 1 or claim 2, characterized in that it is carried out at an ethene/carbon monoxide partial pressure ratio of between 0.80 and 2.5.

4. Process as claimed in any one of claims 1-3, characterized in that it is carried out at a temperature of between 20 and 200°C.

5. Process as claimed in any one of claims 1-4, characterized in that a catalyst composition is used which is based upon a palladium salt of a carboxylic acid, such as palladium acetate, as component (a).

6. Process as claimed in any one of claims 1-5, characterized in that a catalyst composition is used which is based upon an anion of a sulphonic acid with a pKa less than 2 or of a carboxylic acid with a pKa less than 2 as component (b).

7. Process as claimed in claim 6 wherein the sulphonic acid with a pKa less than 2 is p-toluenesulphonic acid.

8. Process as claimed in claim 6 wherein the carboxylic acid with a pKa less than 2 is trifluoroacetic acid.

9. Process as claimed in any one of claims 1-5, characterized in that a catalyst composition is used in which component (b) has been incorporated in the form of a salt chosen from the group formed by zirconium, vanadium, chromium, iron, nickel, copper, cerium, thorium and uranium salts.

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10. Process as claimed in any one of claims 5-9, characterized in that a catalyst composition is used which in addition includes a quinone as component (d).

11. Process as claimed in claim 10 wherein the quinone is 1,4-benzoquinone.

12. Process as claimed in any one of claims 1-11, characterized in that a catalyst composition is used in which component (b) has been incorporated in the form of a main group metal salt and which in addition optionally includes an ether as component (d), on the understanding that the presence of an ether is compulsory when the composition contains an alkali or alkaline earth metal salt as component (b).

13. Process as claimed in claim 12, characterized in that a catalyst composition is used in which component (b) has been incorporated in the form of a salt chosen from the group formed by aluminium, gallium, tin, lead, antimony, lithium, potassium, sodium and magnesium salts.

14. Process as claimed in any one of claims 1-13, characterized in that a catalyst composition is used which includes a component (c) wherein M is phosphorus, wherein the groups R^1 , R^2 , R^3 and R^4 are phenyl groups or substituted phenyl groups and wherein the bivalent organic bridging group R contains three carbon atoms in the bridge.

15. A process for the preparation of polymers, substantially as hereinbefore described with reference to either one of Examples 6 or 8.

16. Polymers whenever prepared by a process as claimed in any one of claims 1 to 15.

DATED this TWENTY-SECOND day of JANUARY 1990
Shell Internationale Research Maatschappij BV

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

JLH/4906M

