Method for the production of a branched macromolecule, the branched macromolecule and uses thereof

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(54) Title: METHOD FOR THE PRODUCTION OF A BRANCHED MACROMOLECULE, THE BRANCHED MACROMOLECULE AND USES THEREOF

(57) Abstract

The invention relates to a process for the preparation of a branched molecule by: a) reacting a nucleus molecule with a compound of a first type which contains a primary and a tertiary isocyanate group; b) reacting the product so obtained with a compound of a second type which contains a first reactive group which can be reacted with a tertiary isocyanate and one or more groups which react with a primary isocyanate and react with a tertiary isocyanate to a lesser extent than the first reactive group, followed by the alternating performance of the steps (c) and (b), c) reacting the product obtained in step (b) with a compound of the first type. The invention also relates to macromolecules obtainable thereby and to the use thereof.

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METHOD FOR THE PRODUCTION OF A BRANCHED MACROMOLECULE, THE BRANCHED MACROMOLECULE AND USES THEREOF

The invention relates to a process for the preparation of a branched macromolecule of the Nth order.

A process for the preparation of a branched macromolecule of the second order is disclosed in US-A-5418301. US-A-5418301 describes a process in which a nucleus molecule which contains one or more hydroxyl groups is brought into contact with a compound which contains one carboxyl group and at least two hydroxyl groups, the amount of said compound being chosen so that the number of carboxyl groups is equal to the number of hydroxyl groups of the nucleus molecule. After the esterification, an amount of the compound containing one carboxyl group and at least two hydroxyl groups is again added, the amount of said compound being chosen so that the number of carboxyl groups is equal to the number of free hydroxyl groups present after the first esterification (hydroxyl groups of the first order). This last step is optionally repeated one or more times. In this way a branched polymer is divergently produced. This method can be performed in one reactor. It is recommended to distil off the water produced in the esterification continuously. A disadvantage of this method is that the carboxyl groups do not react exclusively with the hydroxyl groups present on the macromolecule of the order last formed, but also with hydroxyl groups of the order to be newly

formed and with hydroxyl groups present in the reaction mixture of molecules not yet bound to the macromolecule. As a result, irregularities are produced in the structure of the subsequent orders, which is evident, inter alia, from a molecular weight spread.

The object of the invention is to provide a method in which said disadvantage does not occur or occurs to a lesser extent.

This object is achieved according to the invention by a method which comprises the following steps:

a) reacting a nucleus molecule containing one or more terminal groups composed of a hydroxyl group, a thiol group or an amino group with a molar amount equivalent with respect to terminal groups of a compound of a first type which contains a primary and a tertiary isocyanate group;

b) reacting the product obtained in the preceding step with a compound of a second type which contains a first reactive group which can be reacted with a tertiary isocyanate and one or more groups which react with a primary isocyanate and react with a tertiary isocyanate to a lesser extent than the first reactive group, the amount of the compound of the second type being chosen so that it is the molar equivalent of an amount added in the preceding step of the compound of the first type, followed by the alternating performance of the steps (c) and (b) in such a way that the total number of steps is N and $N \geq 2$;

c) reacting the product obtained in step (b) with a compound of the first type, the amount of the compound of the first type being chosen so that it

is the molar equivalent of the number of less reactive groups added in step (b),

the steps (a), (b) and (c) being performed in the presence of an ionogenic metal complex which contains a metallic element from the groups 3, 4 and 7 of the Periodic System of the Elements and an interchangeable counterion.

The process according to the invention achieves the result that there is formed in one reactor a branched polymer which has a regular structure of successive orders. It has been found that the branched polymer prepared by the method according to the invention has a very limited molecular weight spread.

An advantage of the process according to the invention is that no water or other reaction products have to be removed between the various steps.

Another process for the preparation of a branched polymer having a regular structure of the successive orders is described by Zeng and Zimmerman in J. Am. Chem. Soc. 1996, 118, 5326-5327. The latter describes how two molecules of (4-tert-butylphenoxy)ethanol are coupled under the so called Mitsunobu conditions (being a coupling in the presence of PPh_3 and diethyl azodicarboxylate (DEAD) in THF) to 1-iodobenzyl-3,5-dicarboxylic acid, a branched molecule of the first order being formed. The centre of said molecule is an aryl iodide which is coupled by a Sonogashira reaction in the presence of $Pd(PPh_3)_2Cl_2$, CuI and triethylamine to the acetylene groups of 3,5-diethynylbenzyl alcohol, a branched macromolecule of the second order being formed. The disadvantage of the process described by Zeng and Zimmerman is that the environments in which the two different reaction steps have to be carried out are incompatible with one

another, as a result of which the successive steps cannot be performed in one reactor and in one and the same medium. Another disadvantage of this convergent build-up of a branched macromolecule is that the reaction takes place in the centre of the macromolecule, as a result of which the yield decreases as the number of orders increases. An advantage of the divergent process according to the invention is that the reaction takes place at the outer shell of the macromolecule, as a result of which the yield is independent of the number of orders.

In this description, a branched macromolecule of the Nth order is understood as meaning a macromolecule which has N shells starting from the nucleus molecule, each reaction step adding one shell and N being ≥ 2. The macromolecule therefore contains at least two shells formed in the first two steps (a) and (b). If the macromolecule contains 3 shells, these have been formed in the steps (a), (b) and (c). A macromolecule having four shells has been formed by consecutively performing the steps (a), (b), (c) and (d).

In the process according to the invention, a nucleus molecule containing one or more terminal groups composed of a hydroxyl group, a thiol group or an amino group is brought into contact with a compound of a first type. Suitable nucleus molecules may be composed of an aliphatic, cycloaliphatic or aromatic diol, an aliphatic, cycloaliphatic or aromatic triol, an aliphatic, cycloaliphatic or aromatic tetrol, a sugar alcohol, di(trismethylolpropane) or dipentaerythritol, an α-alkylglucoside, a monofunctional alcohol containing 1-10,000 carbon atoms, or an alcohol

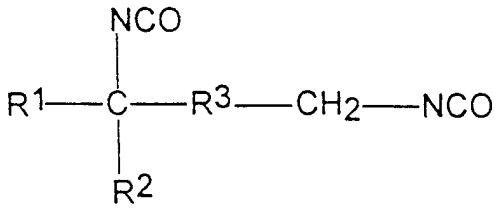
containing a functional group which does not react with an isocyanate containing 1-10,000 carbon atoms.

Suitable nucleus molecules are trimethylolpropane (TMP), pentaerythritol, bis(trimethylolpropane), tris(aminoethyl)amine, bis(aminoethyl)amine, tris(aminopropyl)amine, bis(aminopropyl)amine, bis(hexamethylene)triamine, tetrakis(aminopropyl)-1,4-butanediamine, trisaminononane, 1,4-butanediamine, 1,6-hexanediamine, ethylenediamine, pentaerythritol tetrakis(2-mercapto-acetate), pentaerythritol tetrakis(2-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), 1,6-hexanedithiol, 1,4-butanedithiol and 1,2-ethanedithiol.

Preferably, the nucleus molecule contains 2, 3 or 4 chemically equivalent terminal groups. This has the advantage that the reactivity with the compound of the first type is identical for all terminal groups, thereby promoting a regular structure of the macromolecule. Examples of this are: trimethylolpropane, pentaerythritol, bis(trimethylolpropane), tris(aminoethyl)amine, tris(aminopropyl)amine, tetrakis(aminopropyl)-1,4-butanediamine, trisaminononane, 1,4-butanediamine, 1,6-hexanediamine, ethylenediamine, pentaerythritol tetrakis(2-mercaptoacetate), pentaerythritol tetrakis(2-mercaptopropionate), trimethylolpropane tris(2-mercaptoacetate), trimethylolpropane tris(3-mercaptopropionate), 1,6-hexanedithiol, 1,4-butanedithiol and 1,2-ethanedithiol.

The compound of the first type contains a primary and a tertiary isocyanate group and it preferably contains 4-20 carbon atoms. This is

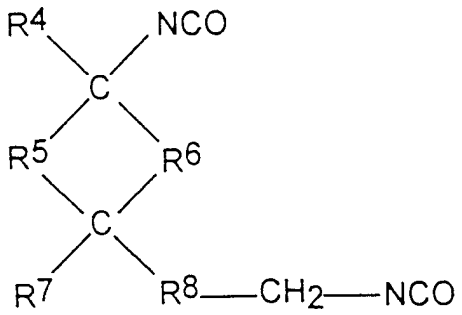
understood as meaning that the compound of the first type is an aliphatic diisocyanate containing one isocyanate group linked to a primary carbon atom and one isocyanate group linked to a tertiary carbon atom. The advantage of such a compound of the first type is that the isocyanate group linked to the primary carbon atom is sterically more accessible than the isocyanate group bound to the tertiary carbon atom, as a result of which the two isocyanate groups have a different reactivity. Such compounds can be represented by the formula (1):



(1)

where R^1 and R^2 contain identical or different (C_1-C_4) alkyl groups and R^3 contains a divalent, optionally branched, saturated aliphatic (C_1-C_{10}) hydrocarbon radical.

Cycloaliphatic diisocyanates can also be used which contain one sterically more accessible isocyanate group linked to a primary carbon atom and one sterically less accessible isocyanate group linked to a tertiary carbon atom. These compounds can be represented by means of formula (2):



(2)

where

- R^4 = a (C_1-C_4) alkyl group,
- R^5 and R^6 = identical or different divalent, optionally branched, saturated aliphatic (C_1-C_3) hydrocarbon radicals,
- R^7 = hydrogen or a (C_1-C_4) alkyl group,
- R^8 = a divalent, optionally branched, saturated aliphatic (C_1-C_6) hydrocarbon radical and
- n = 0 or n = 1.

Examples of suitable diisocyanates are 1,4-diisocyanato-4-methylpentane, 1,5-diisocyanato-5-methylhexane, 3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate, 1,6-diisocyanato-6-methylheptane, 1,5-diisocyanato-2,2,5-trimethylhexane and 1,7-diisocyanato-3,7-dimethyloctane, or 1-isocyanato-1-methyl-4-(4-isocyanato-2-butyl)cyclohexane, 1-isocyanato-1,2,2-trimethyl-3-(2-isocyanatoethyl)cyclopentane, 1-isocyanato-1,4-dimethyl-4-isocyanatomethylcyclohexane, 1-isocyanato-1,3-dimethyl-3-isocyanatomethylcyclohexane, 1-isocyanato-1-n-butyl-3-(4-isocyanato-1-butyl)cyclopentane, 1-isocyanato-1,2-dimethyl-3-ethyl-3-isocyanatomethylcyclopentane. The method of preparation of such diisocyanates is described in, for example, DE-A-3608354, DE-A-3620821 and EP-A-153561.

Preferably, the compound of the first type is 3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate (IMCI) or 1,4-diisocyanato-4-methylpentane.

In the process according to the invention, the nucleus molecule is brought into contact with an equivalent molar amount, with respect to the terminal groups of the nucleus molecule, of the compound of the first type. This achieves the result that only the most reactive isocyanate group reacts with the terminal groups of the nucleus molecule and the reaction proceeds stoichiometrically.

The uncatalysed reaction between the nucleus molecule and a compound of the first type has a selectivity which decreases considerably at higher temperatures if the terminal groups of the nucleus molecule are composed of hydroxyl groups or thiol groups. The selectivity of this reaction is understood as meaning the ratio between the primary isocyanate groups reacted with the terminal groups and the total number of primary isocyanate groups. In general the selectivity of the reaction is high at room temperature, but the reaction rate is relatively low. The reaction is therefore performed in the presence of a catalyst containing an ionogenic metal complex based on a metallic element from the groups III, IV or VII of the Periodic System of the Elements and at least one interchangeable counterion. This achieves the result that the reaction proceeds rapidly at a temperature between room temperature and 100°C and that a high selectivity is also obtained. The reaction is preferably performed in a solvent having a boiling point between room temperature and 100°C, with reflux of

the solvent. The catalysed reaction proceeds virtually quantitatively in 0.5 to 8 hours.

As a result of using the catalyst, the coupling of the diisocyanate to the hydroxyl group, amino group or the thiol group of the nucleus molecule takes place exclusively or virtually exclusively via the most reactive isocyanate group. Surprisingly, the difference in reactivity between the isocyanate groups present in these compounds with a hydroxyl group appeared to be more than a factor of 100.

Suitable metallic elements in the suitable valency are aluminium(III), tin(IV), manganese(III), titanium(III), titanium(IV) and zirconium(IV).

Preferably, tin(IV), titanium(IV), manganese(III) and zirconium(IV) are used.

The number of counterions is between 1 and 4.

In the case of tetravalent metals, it is possible to use, for example, 4 monovalent counterions, 2 divalent counterions, 1 divalent counterion in combination with 2 monovalent counterions or 1 trivalent counterion in combination with 1 monovalent counterion. Preferably, 4 monovalent counterions are used.

In the case of trivalent metals, the number of counterions is between 1 and 3 and, preferably, 3 monovalent counterions are used.

Examples of suitable counterions are halides, preferably chloride, (C_1-C_{20}) alkoxides, preferably (C_1-C_8) alkoxide, (C_2-C_{20}) carboxylates, preferably (C_2-C_8) carboxylates, enolates of, preferably, 2,4-pentanedione (acetylacetonates), and alkyl esters of malonic acid and acetylacetic acid, phenolates, naphthenates, cresylates and mixtures of said counterions.

Suitable catalysts are, for example, aluminium(III) acetate, aluminium(III) acetylacetonate, aluminium(III) 2,2,6,6-tetramethyl-3,5-heptanedionate, aluminium(III) ethoxide, aluminium(III) isopropoxide, aluminium(III) sec-butoxide, aluminium(III) tert-butoxide, tin(IV) chloride, tin(IV) bromide, tin(IV) iodide, tin(IV) acetate, tin(IV) bis(acetylacetonate) dichloride, tin(IV) bis(acetylacetonate) dibromide, manganese(III) acetate, manganese(III) acetylacetonate, manganese(III) fluoride, titanium(IV) chloride, titanium(IV) bromide, titanium(IV) methoxide, titanium(IV) ethoxide, titanium(IV) isopropoxide (TYZOR TPT™), titanium(IV) propoxide, titanium (IV) butoxide (TYZOR TPT™), titanium(IV) 2-ethylhexoxide (TYZOR TOT™), titanium(IV) acetylacetonate, titanium(IV) bis(acetylacetonate) diisopropoxide (TYZOR AA™), titanium(IV) bis(ethylacetoacetato) diisopropoxide, titanium(IV) (triethanolaminato) isopropoxide (TYZOR TE™), zirconium(IV) chloride, zirconium(IV) bromide, zirconium(IV) acetate, zirconium(IV) 2-ethylhexanoate, zirconium(IV) ethoxide, zirconium(IV) butoxide, zirconium(IV) tert-butoxide, zirconium(IV) citrate ammonium complex, zirconium(IV) isopropoxide, zirconium(IV) propoxide, zirconium(IV) acetylacetonate and zirconium(IV) trifluoroacetylacetonate.

Preferably, titanium(IV) butoxide, zirconium(IV) acetylacetonate, zirconium(IV) butoxide, tin(IV) acetate, manganese(III) acetylacetonate, titanium(IV) isopropoxide, zirconium(IV) 2-ethylhexanoate and tin(IV) chloride are used.

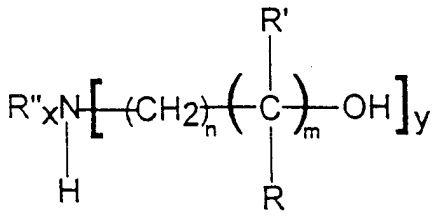
The catalyst complex may also contain one or more neutral elements, such as, for example, alkyl cyanide, crown ether, (poly)ether, such as, for

example, polytetrahydrofuran, polyethylene glycol or tetrahydrofuran, dialkyl sulphide or tertiary amine.

The amount of catalyst is generally between 0.01 and 3% by weight (relative to the compound which can react with isocyanate groups and the compound which contains isocyanate groups).

In step (b), the product obtained in the preceding step is brought into contact with a compound of a second type which contains a first reactive group which can be reacted with a tertiary isocyanate, and one or more groups which react with a primary isocyanate and react with the tertiary isocyanate to a lesser extent than the first reactive group. This achieves the result that the groups which react with the tertiary isocyanate react with it completely. The 'preceding step' is understood as meaning reaction step (a) if (b) is performed for the first time. For all the subsequent times which (b) is performed, step (c) is the preceding step.

Suitable compounds of the second type are compounds which contain 4 to 40 carbon atoms and belong to the group comprising the amino alcohols or amino thiols which contain one primary or secondary amino group as reactive group and at least one hydroxyl group or thiol group as less reactive group. Polyols containing one reactive hydroxyl group and at least one less reactive hydroxyl group are also suitable compounds of the second type. Preferably, the compound of the second type is tris(methylol)methylamine (TRIS) or monoalkanolamines or bisalkanolamines of the formula 3:



(3)

where x = 0 or 1, y = 2-x, n = 1 or 2, m = 0 or 1, R = H or alkyl C_1-C_4, R' = (C_1-C_4) alkyl and R'' = (C_1-C_{20}) alkyl. Examples thereof are (N-alkyl)ethanolamine, N-alkyl)isopropanolamine, diethanolamine or diisopropanolamine. The advantage of using amines is that they react virtually quantitatively with the tertiary reactive isocyanate groups of the diisocyanate without this reaction needing the presence of a catalyst or being adversely influenced by the presence of the catalyst. This achieves the result that no catalyst has to be removed between the various steps. The quantity of the compound of the second type is chosen so that it is the molar equivalent of the amount used in the preceding step of the compound of the first type.

In step (c), the product obtained in step (b) is brought into contact with a compound of the first type. The reaction between the primary isocyanate group of the compound of the first type and one or more groups of the compound of the second type which react with a primary isocyanate (the hydroxyl groups or thiol groups) is performed in the presence of the abovementioned catalyst. The temperature at which said reaction is performed is generally between room temperature and 100°C. The amount of the compound of the first type is chosen so that it is the molar equivalent

of the number of less reactive groups added in step (b).

The steps (a), (b) and (c) are performed in the presence of the abovementioned ionogenic metal complex which contains a metallic element from the groups III, IV or VII of the Periodic System of the Elements and an interchangeable counterion. Preferably, the (metallic) element in the process according to the invention is zirconium(IV). The counterion is preferably acetylacetonate, butoxide or 2-ethylhexanoate.

In the process according to the invention, the compounds of the second type which are used in the steps (b) are the same or different. According to a preferred embodiment of the process according to the invention, the compound of the second type is different in at least two steps (b). This can achieve the result that a cavity is formed within the macromolecule. For this purpose, the compounds of the second type can differ from one another in at least two steps (b) in different manners.

A first method of creating a cavity within the macromolecule is by using at least once a compound of the second type having only one less reactive group. In order to obtain a highly branched macromolecule, a compound of the second type is generally used in which at least two groups are present which can be reacted with a primary isocyanate group. However, by performing step (b) one or more consecutive times with a compound of the second type in which only one group is present which can be reacted with a primary isocyanate group, one or more shells having fewer branches are formed. As a result a cavity is produced in the macromolecule.

The size of said cavity can be chosen by means of the number of times that a compound of the second type having only one group which can be reacted with a primary isocyanate is used consecutively in step (b).

A second method of creating a cavity within the highly branched macromolecule is to use at least once in step (b) a compound of the second type, the distance between the groups which can be reacted with primary and tertiary isocyanate being greater than said distance in the compounds of the second type which are used in the other steps (b).

A combination of the first and the second method can also be used to create a cavity to size within the macromolecule. The advantage of cavities to size is that selectively determined compounds can be included therein and also that diffusion to and from the cavity can be influenced thereby.

In a preferred embodiment of the method according to the invention, the compound of the second type contains in at least one of the steps (b) at least one functional group which does not react with isocyanate or has an interfering effect on the reaction between isocyanate and the groups which can be reacted with isocyanate. The functional group which does not react with isocyanate is preferably chosen from the series of compounds containing an ethylenic or ethynic unsaturation, a crown ether or from trialkylphosphine, triarylphosphine, pyridine, bipyridine, phenanthroline, trisalkylamine, dialkyl sulphide, guanidine or alkyl-imidazoline, benzoquinone, anthraquinone, hydroxybenzophenone, ketones and aldehydes or blocked amines, alcohols, thiols and acids. This achieves the result that additional functional groups are incorporated

which can interact with guest molecules in an internal cavity optionally introduced into the macromolecule, if necessary after deblocking. Guest molecules may be metal ions or metal complexes, dyes, peroxides, photoactive organic or inorganic compounds, organic bases or acids, or compounds having a catalytic or pharmaceutical action.

In a preferred embodiment of the process according to the invention, the compound of the first type is replaced in the step (c) to be performed last by a compound which contains only one primary isocyanate group. This achieves the result that the isocyanate groups react with the terminal groups of the product obtained in the last step (b) and the product obtained in this way no longer contains any isocyanate groups. Examples of such monoisocyanates are: alkylisocyanates (C_2-C_{20}), optionally substituted, branched or unsaturated, and 3-isocyanates of propyltri(m)ethoxysilane. If the macromolecule contains, for example, 3 shells, these have been formed in the steps (a), (b) and step (c) as described above.

In another preferred embodiment of the process according to the invention, the compound of the second type in the last time that step (b) is performed is replaced by a derivatizing agent: a compound which contains one reactive group which can be reacted with a tertiary isocyanate. If the macromolecule contains, for example, 2 shells, these have been formed in step (a) and in step (b) as described above. This prevents, for example, a molecular weight increase occurring after the reaction as a result, for example, of hydrolysis of the isocyanate groups or of urea formation. The terminal groups of the macromolecule also determine the nature thereof. For example, the solubility of the

macromolecule can be influenced by a suitable choice of the terminal groups. Suitable derivatization agents for performing the last step (b) of the reaction are, for example, diethylamine, mono(C_2-C_{40})alkylamines and bis(C_1-C_{40})alkylamines, optionally substituted or unsaturated, 3-aminopropylsilane derivatives, amino acids (natural and synthetic) and amino acid derivatives, and alcohols (C_1-C_{20}), optionally substituted or unsaturated.

The reactions (b) and (c) are preferably performed under nitrogen.

All the reactions are preferably performed in a solvent in which all the components are readily soluble. Suitable solvents are solvents having a low viscosity which do not themselves react with isocyanate groups. In order to prevent an uncontrolled build-up of the branched macromolecule as a result of hydrolysis of isocyanates and urea formation, it is advisable to dry the solvent beforehand using, for example, a molecular sieve type 3A.

The invention also relates to a branched macromolecule obtainable by the process according to the invention. Branched macromolecules based on isocyanates are disclosed in DE-A-195 240 045. This describes dendritic macromolecules which are formed by coupling, to a nucleus molecule having at least 2 functional groups B^1, a molecule AB_n to every functional group B^1 and by coupling a subsequent AB_n group to every group B, and so forth, n being at least 2 and A being an isocyanate group. It is not stated anywhere in DE-A-195 240 045 that A is a diisocyanate containing a primary and a tertiary isocyanate.

The advantage of the branched molecule according to the invention (containing primary and tertiary isocyanate) is the lower polydispersity.

Preferably, the polydispersity of the macromolecule according to the invention is less than 1.5. More preferably it is less than 1.1. Still more preferably, the polydispersity is less than 1.05.

The disadvantage of the process described in DE-A-195 240 045 is that a lower polydispersity can be obtained only by using protective and deprotective steps.

A further advantage of the process according to the invention is that the preparation can be stopped after step (b) or after step (c), whereas the process described in DE-A-195 240 045 always terminates with groups which can react with isocyanate.

The invention also relates to the use of said macromolecule as a crosslinking agent, as a lubricating agent, as a catalyst or catalyst support, as a photosensitizer, as a dye carrier and in pharmaceuticals.

Example I

A branched macromolecule of the second order was prepared in the following manner: 2 ml of a 0.075 M solution of zirconium(IV) acetylacetate in tetrahydrofurane (THF) was added to 25.00 ml of a 0.200 M solution of trismethylolpropane (TMP, 99+%, Aldrich). 25.00 ml of a 0.600 M solution of 3(4)-isocyanomethyl-1-methylcyclohexyl isocyanate (IMCI) (99+%, Bayer) were then slowly added at room temperature. The mixture was quickly heated to reflux temperature (58°C) with continuous stirring. After 4 hours of stirring at the

reflux temperature, the mixture was cooled, after which 10.00 ml of a 1.500 M solution of diethylamine (DA) in THF were slowly added. After 30 minutes, a sample of this mixture was taken, diluted with HPCL-grade THF (1:5) and then directly injected into a gel permeation chromatography column. The result is shown in the lowermost line of Figure 1. The sharp peak at 32 min corresponds to the ideal "trimeric" structure. A signal originating from unreacted IMCI (35.5 min) is no longer visible. The peak at 30.5 min having an area of less than 2% of the peak at 35.5 can be attributed to a "pentameric" structure which is composed of 2 TMP units and 5 IMCI/DA units. In this defect structure, one of the five IMCI units has reacted both via the primary isocyanate group and the tertiary isocyanate group. The peaks at 32.5 and 34 min, which are also small, originate from incomplete structures composed of one TMP unit and, respectively, only 2 or 1 IMCI units. The molecular weight spread, expressed in the polydispersity (= Mw/Mn) of the whole is 1.03, which means that virtually all the molecules have an ideally branched structure. The polydispersity was determined from the GPC measurements, polystyrene being used as standard.

The reaction mixture was evaporated down further and a colourless, glassy material was obtained.

Example II

A branched macromolecule of the fourth order was prepared in the following manner: the same procedure was followed as for the preparation of a branched macromolecule of the first order, except that 50.00 ml of a 0.6 M solution of diethanolamine in THF was added instead of 10 ml of diethylamine. After

stirring for 16 hours, 11.652 g IMCI and 4.0 ml of the 0.075 M solution of zirconium(IV) acetylacetate in THF were added and heating was carried out to the reflux temperature (58°C). After stirring for 4 hours at reflux temperature, the mixture was cooled, after which 20 ml of a 1.500 M solution of diethylamine (2.2 g) in THF were slowly added. After 30 minutes, a sample of this mixture was taken, diluted with HPCL grade THF (1:5) and directly thereafter injected into a gel permeation chromatography column. The result is shown in the centre line of Figure 1. Around the sharp peak at approximately 30 min, which originates from the ideally branched macromolecule, small shoulders are visible of material having a higher and a lower molecular weight. The polydispersity of the macromolecule formed was 1.06. After evaporating the reaction mixture down, a colourless, glassy material was again obtained. This macromolecule is of the fourth order.

Example III

A branched macromolecule of the sixth order (G3) was prepared in the following manner: the same procedure was followed as for the preparation of a branched macromolecule of the second order, except that 25.00 ml of a 0.6 M solution of diethanolamine in THF were added instead of 20 ml of diethylamine. This mixture was stirred for 16 hours at room temperature. Then 5.827 g of IMCI and 2.0 ml of the 0.075 M solution of zirconium(IV) acetylacetate in THF were added and heating was carried out to reflux temperature (58°C). After stirring for 4 hours at the reflux temperature, the mixture was cooled, after which 40 ml of a 1.500 M solution of diethylamine (4.4 g) in THF were slowly

added. After 30 minutes, a sample was taken of this mixture, diluted with HPCL-grade THF (1:5) and then directly injected into a gel permeation chromatography column. The result is shown in the uppermost line of Figure 1. In addition to the sharp peak at approximately 28 min shown in Figure 2, which originates from the ideally branched macromolecule, a small peak is visible at 27 min originating from material having a higher molecular weight. The polydispersity of the whole was 1.07. After evaporating down, a colourless, glassy material was obtained.

C L A I M S

1. Process for the preparation of a branched macromolecule of the Nth order, comprising the following steps:

a) reacting a nucleus molecule containing one or more terminal groups composed of a hydroxyl group, a thiol group or an amino group with a molar amount equivalent with respect to terminal groups of a compound of a first type which contains a primary and a tertiary isocyanate group;

b) reacting the product obtained in the preceding step with a compound of a second type which contains a first reactive group which can be reacted with a tertiary isocyanate and one or more groups which react with a primary isocyanate and react with a tertiary isocyanate to a lesser extent than the first reactive group, the amount of the compound of the second type being chosen so that it is the molar equivalent of an amount added in the preceding step of the compound of the first type, followed by the alternating performance of the steps (c) and (b) in such a way that the total number of steps is N and $N \geq 2$;

c) reacting the product obtained in step (b) with a compound of the first type, the amount of the compound of the first type being chosen so that it is the molar equivalent of

the number of less reactive groups added in step (b),

wherein the steps (a), (b) and (c) are performed in the presence of an ionogenic metal complex which contains a metallic element from the groups III, IV and VII of the Periodic System of the Elements and an interchangeable counterion.

2. Process according to Claim 1, wherein the nucleus molecule contains 2, 3 or 4 chemically equivalent terminal groups.

3. Process according to Claim 2, wherein the nucleus molecule is trimethylolpropane, pentaerythritol, bis(trimethylolpropane), tris(aminoethyl)amine, tris(aminopropyl)amine, tetrakis(aminopropyl) 1,4-butanediamine, trisaminononane-1,4-butanediamine, 1,6-hexanediamine or ethylenediamine.

4. Process according to Claim 3, wherein the compound of the first type is 3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate or 1,4-diisocyanato-4-methylpentane.

5. Process according to one of Claims 1-4, wherein the compound of the second type is (N-alkyl)ethanolamine, (N-alkyl)isopropanolamine, diethanolamine, diisopropanolamine or trismethylolmethylamine, the alkyl group of which contains 1-20 carbon atoms.

6. Process according to one of Claims 1-5, wherein the metallic element is zirconium(IV).

7. Process according to one of Claims 1-6, wherein the counterion is chloride acetate, acetylacetonate, butoxide or 2-ethylhexanoate.

8. Process according to one of Claims 1-7, wherein the compound of the second type is different in at least two steps (b).

9. Process according to one of Claims 1-8, wherein the compound of the second type in at least one of the steps (b) contains at least one functional group which does not react with isocyanate.

10. Process according to Claim 9, wherein the functional group which does not react with isocyanate is chosen from the series of compounds having an ethylenic or ethynic unsaturation, a crown ether or from trisalkylphosphine, trisarylphosphine, pyridine, bipyridine, phenanthroline, trisalkylamine, dialkyl sulphide, guanidine, alkylimidazoline, benzoquinone, anthraquinone, hydroxybenzophenone, ketones and aldehydes, or blocked amines, alcohols, thiols and acids.

11. Process according to one of more of Claims 1-10, wherein the compound of the first type in the last step (c) to be performed is replaced by a compound which contains only one reactive group which can be reacted with the terminal groups of the product obtained in step (b).

12. Process according to one of Claims 1-11, wherein the compound of the second type in the last time that step (b) is performed is replaced by a compound which contains one reactive group which can be reacted with a tertiary isocyanate.

13. Branched macromolecule obtainable from the process according to one of Claims 1-12.

14. Use of the macromolecule according to Claim 13 in a coating as a crosslinking agent.

15. Use of the macromolecule according to Claim 13 as a lubricating agent.

16. Use of the macromolecule according to Claim 13 as a catalyst or catalyst support.

17. Use of the macromolecule according to Claim 13 in pharmaceuticals.
18. Use of the macromolecule according to Claim 13 as photosensitizer.
19. Use of the macromolecule according to Claim 14 as dye carrier.

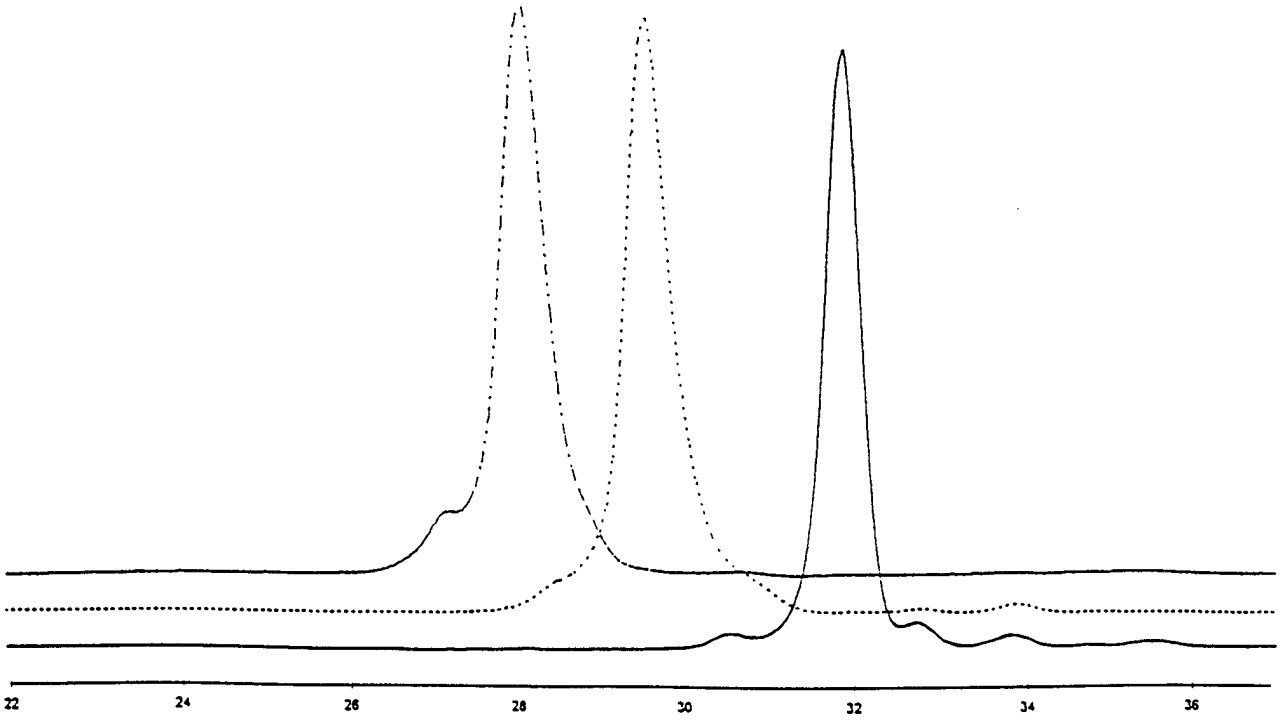


Figure 1: GPC chromatograms of branched macromolecules on the basis of TMP, IMCI and DEA of (from bottom to top) of the second, fourth and sixth order, with calculated polydispersities (Mw/Mn) of 1.03, 1.06 and 1.07, respectively.

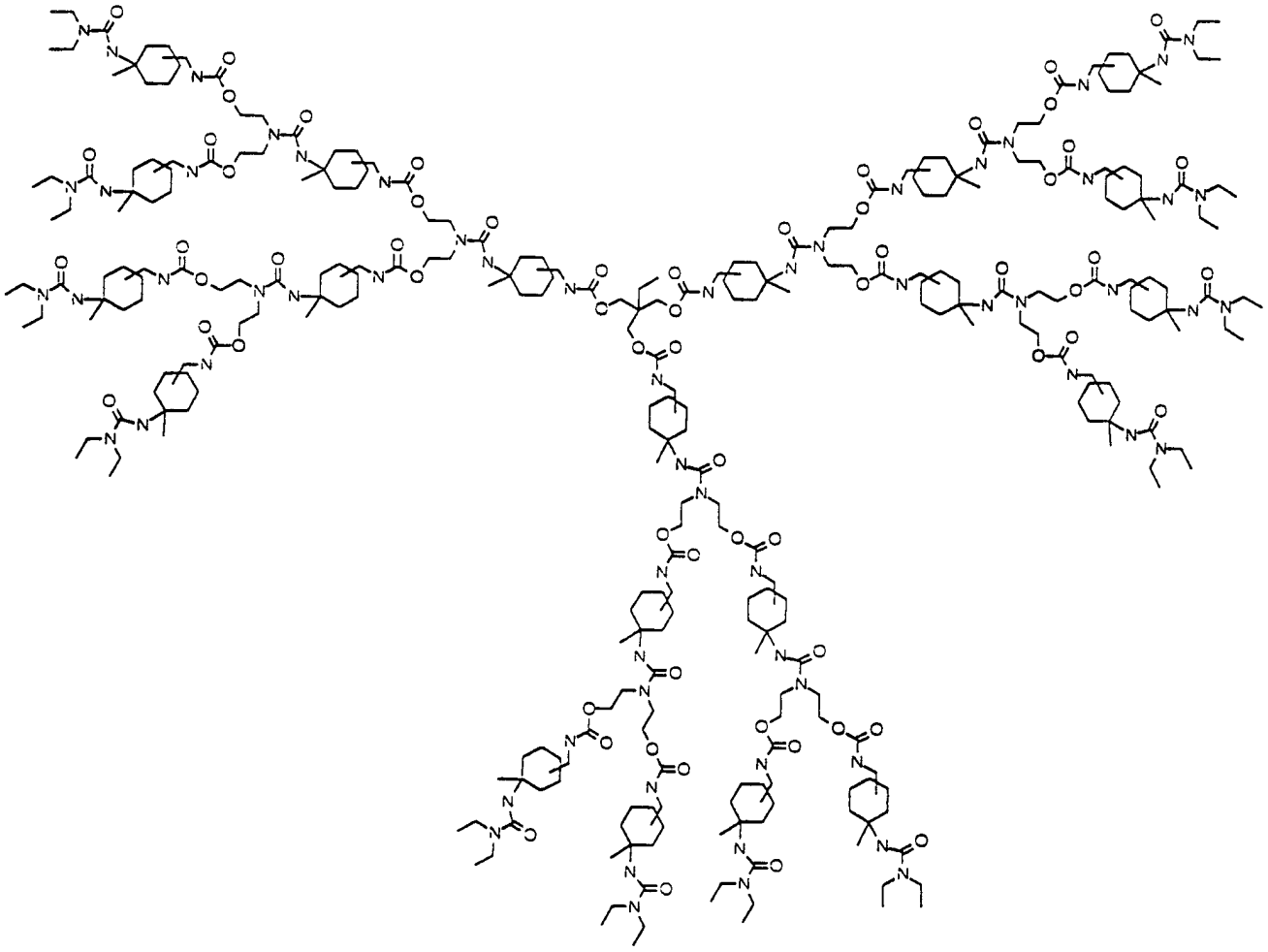


Figure 2: Structure of the branched sixth-order macromolecule on the basis of TMP, IMCI and DEA, the terminal group being modified with diethyl amine.

INTERNATIONAL SEARCH REPORT

Ir ational Application No
PCT/NL 98/00284

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G83/00 C08G18/73 C08G18/75 C08G18/22 C08G18/32

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)
IPC 6 C08G C09D C08L

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 195 24 045 A (BASF AG) 2 January 1997 cited in the application see claims 1,2,4,10,11,13 see page 3, line 53 - line 61	1
A	WO 97 36857 A (WEIS CLAUS ;NEWKOME GEORGE R (US); UNIV SOUTH FLORIDA (US)) 9 October 1997 see claims 1,2,15,16	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of theinternational search	Date of mailing of the international search report
9 July 1998	17/07/1998

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In ational Application No
PCT/NL 98/00284

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