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(54) **METHOD OF PRODUCING A POLYMERIC MATERIAL, POLYMER, MONOMERIC COMPOUND AND METHOD OF PREPARING A MONOMERIC COMPOUND**

VERFAHREN ZUR HERSTELLUNG EINES POLYMERMATERIALS, POLYMER, MONOMERE VERBINDUNG UND VERFAHREN ZUR HERSTELLUNG EINER MONOMEREN VERBINDUNG
MATIÈRES POLYMÉRIQUES ET PROCÉDÉS SERVANT À FABRIQUER CELLES-CI

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- (56) References cited:
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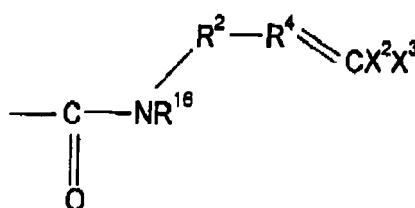
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Description

[0001] This invention relates to polymeric materials, methods of manufacturing said polymeric materials, and associated monomers.

[0002] International Publications WO 00/06610, WO 00/06533, WO 00/06658, WO 01/36510, WO 01/40874 and WO 01/74919, the contents of all of which are herein incorporated by reference, discloses a class of polymers obtained from the polymerisation of a number of compounds which possess one or more dienyl end groups. The polymers possess or promise a variety of useful and exciting properties, such as ease of polymerisation, and the ability to "tailor" the properties of the polymer by variation of the "core" group that the end group(s) is attached to. However, the present inventors have found that difficulties can be experienced in polymerising some monomers of the type taught in WO 00/06610. Accordingly, the present inventors have devised improved polymeric systems which, in at least some of their embodiments, enable facile polymerisation to take place and provide polymeric materials exhibiting advantageous and improved properties.

[0003] According to a first aspect of the invention there is provided a method of producing a polymeric material, said method including the step of subjecting a starting material which includes a group of sub-formula (XIII)



(XIII)

where R^{16} is selected from hydrogen, halo, nitro, hydrocarbonyl, optionally substituted or interposed with functional groups, or $-\text{R}^3-\text{R}^5=\text{C} \text{Y}^2 \text{Y}^3$;

R^2 and R^3 are independently selected from $(\text{C} \text{R}^6 \text{R}^7)_n$ or a group $\text{C} \text{R}^8 \text{R}^9$, $\text{C} \text{R}^6 \text{R}^7 \text{C} \text{R}^8 \text{R}^9$ or $\text{C} \text{R}^8 \text{R}^9 \text{C} \text{R}^6 \text{R}^7$ where n is 0, 1 or 2, R^6 and R^7 are independently selected from hydrogen or alkyl, and either one of R^8 or R^9 is hydrogen and the other is an electron withdrawing group, or R^8 or R^9 together form an electron withdrawing group; and R^4 and R^5 are independently selected from $\text{C} \text{H}$ or $\text{C} \text{R}^{10}$ where $\text{C} \text{R}^{10}$ is an electron withdrawing group, and X^2 and X^3 , and, if present, Y^2 and Y^3 are each a C_1 to C_4 alkyl group; to conditions under which polymerisation of the starting material occurs.

[0004] For the avoidance of doubt, a resulting polymeric chain can be any polymeric chain comprising repeat units, and a polymer may comprise one or more polymeric chains, which may be cross-linked.

[0005] The present inventors have recognised that certain difficulties can be encountered in polymerising some of the species disclosed in WO 00/06610. Furthermore, the present inventors have recognised that the difficulties can be due to certain side reactions which can occur in competition with the desired diene polymerisation reaction. In particular, the present inventors have recognised that in diene polymerisation schemes of the type disclosed in WO 00/06610, the diene groups need to be activated in order to make them susceptible to radical polymerisation. This activation is manifest by a reduction in electron density in the carbon-carbon double bonds caused by the presence of electron withdrawing groups near or actually adjacent to the diene groups. However, when dienes are activated in this way, another reaction mechanism can occur which involves hydrogen atoms attached to the carbon atoms adjacent to the diene bonds. These hydrogen atoms are so called allylic hydrogens, and can take part in unwanted dimerisation reactions. Monomers which less strongly electron withdrawing with respect to the carbon-carbon double bonds, such as dienyl amides, are especially susceptible to unwanted allylic hydrogen reactions occurring. Very surprisingly, the present inventors have found that the desired polymerisation reaction can be favoured by varying the nature of the substituents attached to the terminal carbon atoms of the dienyl group. In particular, it has been found that the use of substituents in these positions which are not taught by WO 00/06610 can provide improved polymerisation. Without wishing to be bound by any particular theory, it is believed that radical intermediates associated with the desired polymerisation reaction may be stabilised by the terminal carbon substituents, and/or radical intermediates, associated with the unwanted allylic side reaction may be destabilised by the terminal carbon substituents.

[0006] Polymers of the invention can be easily and conveniently polymerised, in at least some instances without the presence of an initiator, adhere very effectively to substrates, and act as a substrate itself upon which other substances can be deposited and adhered.

[0007] Generally, X^2 , X^3 , Y^2 (when present) and Y^3 (when present) stabilise desired free radical intermediates and/or destabilise unwanted free radical intermediates.

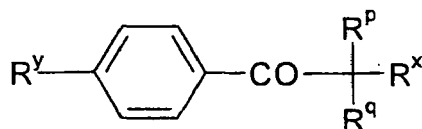
[0008] X^2 , X^3 , Y^2 and Y^3 are C_1 to C_4 alkyl groups; especially methyl or ethyl. Very surprisingly, it has been found that

embodiments in which X^2 , X^3 , Y^2 and/or Y^3 are C_1 to C_4 alkyl groups are able to polymerise on exposure to radiation without the presence of an initiator.

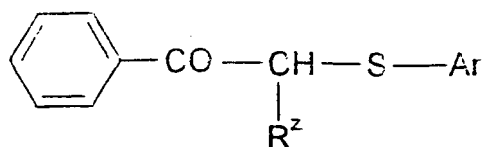
[0009] In one important range of embodiments, the group of the sub-formula (I) includes the group $-R^3-R^5=CY^2Y^3$, the polymerisation is a cyclopolymerisation reaction, and at least one of (a) R^1 or (b) R^2 and R^3 or (c) R^4 and R^5 includes an electron withdrawing group which is able to activate a cyclopolymerisation reaction.

[0010] Conditions under which polymerisation occurs may comprise the application of radiation, such as UV radiation, where necessary in the presence of a photoinitiator (but preferably without an initiator present), the application of heat (which may be in form of IR radiation), where necessary in the presence of an initiator, by the application of other sorts of initiator such as chemical initiators, or by initiation using an electron beam. The expression "chemical initiator" as used herein refers to compounds which can initiate polymerisation such as free radical initiators and ion initiators such as cationic or anionic initiators as are understood in the art. Radiation or electron beam induced polymerisation is suitably effected in the substantial absence of a solvent. As used herein, the expression "in the substantial absence of solvent" means that there is either no solvent present or there is insufficient solvent present to completely dissolve the reagents, although a small amount of a diluent may be present to allow the reagents to flow.

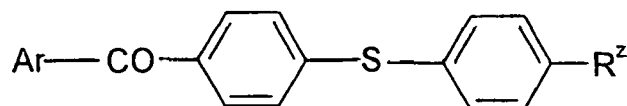
[0011] Preferably, the starting materials polymerise under the influence of ultraviolet radiation or both. Polymerisation may take place either spontaneously or in the presence of a suitable initiator. Examples of suitable initiators include 2, 2' - azobisisobutyronitrile (AIBN), aromatic ketones such as benzophenones in particular acetophenone; chlorinated acetophenones such as di- or tri-chloroacetophenone; dialkoxyacetophenones such as dimethoxyacetophenones (sold under the trade name "Irgacure 651") dialkylhydroxyacetophenones such as dimethylhydroxyacetophenone (sold under the trade name "Darocure 1173"); substituted dialkylhydroxyacetophenone alkyl ethers such compounds of formula



where R^y is alkyl and in particular 2, 2-dimethylethyl, R^x is hydroxyl or halogen such as chloro, and R^p and R^q are independently selected from alkyl or halogen such as chloro (examples of which are sold under the trade names "Darocure 1116" and "Trigonal P1"); 1-benzoylcyclohexanol-2 (sold under the trade name "Irgacure 184"); benzoin or derivatives such as benzoin acetate, benzoin alkyl ethers in particular benzoin butyl ether, dialkoxybenzoin such as dimethoxybenzoin or deoxybenzoin; dibenzyl ketone; acyloxime esters such as methyl or ethyl esters of acyloxime (sold under the trade name "Quantaqure PDO"); acylphosphine oxides, acylphosphonates such as dialkylacylphosphonate, keto-sulphides for example of formula



where R^z is alkyl and Ar is an aryl group; dibenzoyl disulphides such as 4, 4'-dialkylbenzoyldisulphide; diphenyldithiocarbonate; benzophenone; 4, 4'-bis (N, N-dialkylamino) benzophenone; fluorenone; thioxanthone; benzil; or a compound of formula



where Ar is an aryl group such as phenyl and R^z is alkyl such as methyl (sold under the trade name "Speedcure BMDS").

[0012] As used herein, the term "alkyl" refers to straight or branched chain alkyl groups, suitably containing up to 20 and preferably up to 6 carbon atoms. The term "alkenyl" and "alkynyl" refer to unsaturated straight or branched chains which include for example from 2-20 carbon atoms, preferably from 2 to 6 carbon atoms. Chains may include one or more double to triple bonds respectively. In addition, the term "aryl" refers to aromatic groups such as phenyl or naphthyl.

[0013] The term "hydrocarbyl" refers to any structure comprising carbon and hydrogen atoms. For example, these may be alkyl, alkenyl, alkynyl, aryl such as phenyl or naphthyl, arylalkyl, cycloalkyl, cycloalkenyl or cycloalkynyl. Suitably they will contain up to 20 and preferably up to 10 carbon atoms. The term "heterocyclic" includes aromatic or non-aromatic

rings, for example containing from 4 to 20, suitably from 5 to 10 ring atoms, at least one of which is a heteroatom such as oxygen, sulphur or nitrogen. Examples of such groups include furyl, thienyl, pyrrolyl, pyrrolidinyl, imidazolyl, triazolyl, thiazolyl, tetrazolyl, oxazolyl, isoxazolyl, pyrazolyl, pyridyl, pyrimidinyl, pyrazinyl, pyridazinyl, triazinyl, quinolinyl, isoquinolinyl, quinoxalinyl, benzthiazolyl, benzoxazolyl, benzothienyl or benzofuryl.

[0014] The term "functional group" refers to reactive groups such as halo, cyano, nitro, oxo, $C(O)_nR^e$, OR^e , $S(O)_tR^e$, NR^fR^g , $OC(O)NR^fR^g$, $C(O)NR^fR^g$, $OC(O)NR^fR^g$, $-NR^7C(O)_nR^6$, $-NR^eCONR^fR^g$, $-C=NOR^e$, $-N=CR^fR^g$, $S(O)_tNR^fR^g$, $C(S)_nR^e$, $C(S)OR^e$, $C(S)NR^fR^g$ or $-NR^fS(O)_tR^e$ where R^e , R^f and R^g are independently selected from hydrogen or optionally substituted hydrocarbyl, or R^f and R^g together form an optionally substituted ring which optionally contains further heteroatoms such as $S(O)_s$, oxygen and nitrogen, n is an integer of 1 or 2, t is 0 or an integer of 1-3. In particular the functional groups are groups such as halo, cyano, nitro, oxo, $C(O)_nR^e$, OR^e , $S(O)_tR^e$, NR^fR^g , $OC(O)NR^fR^g$, $C(O)NR^fR^g$, $OC(O)NR^fR^g$, $-NR^7C(O)_nR^6$, $-NR^eCONR^fR^g$, $-NR^eCSNR^fR^g$, $C=NOR^e$, $-N=CR^fR^g$, $S(O)_tNR^fR^g$, or $-NR^fS(O)_tR^e$ where R^e , R^f and R^g , n and t are as defined above.

[0015] The term "heteroatom" as used herein refers to non-carbon atoms such as oxygen, nitrogen or sulphur atoms. Where the nitrogen atoms are present, they will generally be present as part of an amino residue so that they will be substituted for example by hydrogen or alkyl.

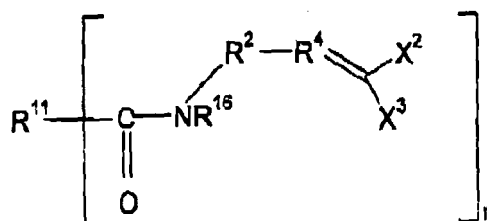
[0016] The term "amide" is generally understood to refer to a group of formula $C(O)NR^eR^f$ where R^e and R^f are hydrogen or an optionally substituted hydrocarbyl group. Similarly, the term "sulphonamide" will refer to a group of formula $S(O)_2NR^eR^f$.

[0017] The nature of any electron withdrawing group or groups additional to the amide moiety used in any particular case will depend upon its position in relation to the double bond it is required to activate, as well as the nature of any other functional groups within the compound. The term "electron withdrawing group" includes within its scope atomic substituents such as halo, e.g. fluoro, chloro and bromo.

[0018] Where R^{10} is an electron withdrawing group, it is suitably acyl such as acetyl, nitrile or nitro.

[0019] Suitable groups R^a include hydrogen or methyl, in particular hydrogen.

[0020] A preferred group of the compounds for use in the method of the invention is a compound of structure (XIV)

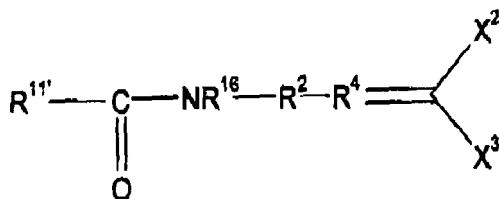


(XIV)

where X^1 , X^2 , X^3 , R^1 , R^2 , R^4 , and the dotted bonds are as defined in relation to formula (I) above, r is an integer of 1 or more, and R^{11} is a bridging group, an optionally substituted hydrocarbyl group, a perhaloalkyl group, a siloxane group or an amide, of valency r .

[0021] Where in the compound of formula (XIV) r is 1, compounds can be readily polymerised to form a variety of polymer types depending upon the nature of the group R^{11} . Examples of groups which are commonly found in polymer technology are included below in Table 1.

[0022] Monomers of this type may be represented as structure (XV)



(XV)

and where X^2 , X^3 , Y^2 , Y^3 , R^2 , R^3 , R^4 and R^{16} are as previously defined, and $R^{11'}$ is an optionally substituted hydrocarbyl group, a perhaloalkyl group, a siloxane group or an amide.

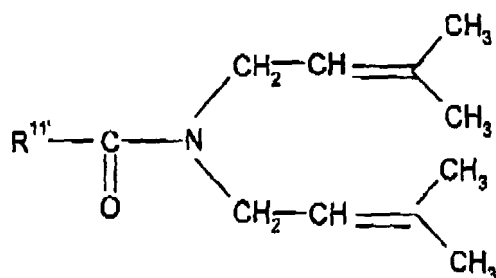
[0023] In particular, R^{11} or $R^{11'}$ may be an optionally substituted alkyl, alkenyl, alkynyl or aryl group, wherein the optional substituents may be selected from halogen, hydroxyl, carboxy or salts thereof or acyloxy.

[0024] In structures of compounds (XIV) and (XV), R^{11} or $R^{11'}$ may comprise a straight or branched chain hydrocarbyl group, optionally substituted or interposed with functional groups.

[0025] Preferably, R^{11} or $R^{11'}$ is an optionally substituted hydrocarbyl group having four or more carbon atoms. R^{11}

or R^{11'} may be a straight or branched chain alkyl group having four or more carbon atoms.

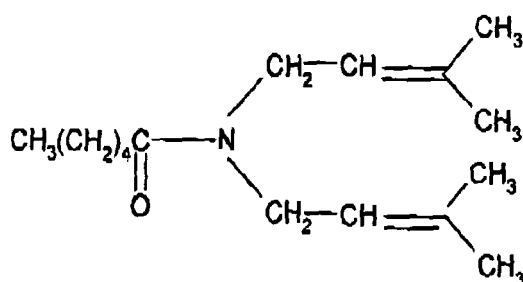
[0026] A preferred class of compounds of formula (III) are those of formula (IV)



(IV)

15 where R^{11'} is as defined above.

[0027] The compound of formula (IV) may be of a compound of formula (V)



(V)

30 **[0028]** Alternatively, R¹¹ or R^{11'} may comprise a perhaloalkyl group, for example of from 1 to 3 carbon atoms such as a perhalomethyl group, in particular perfluoromethyl.

[0029] The invention may also be applied to other sorts of polymers; for example, where in the compounds of formula (XIV), r is greater than one, polymerisation can result in polymer networks. Particular examples are compounds of formula (XIV) as defined above, where R¹¹ is a bridging group and r is an integer of 2 or more, for example from 2 to 8 and preferably from 2 - 4.

35 **[0030]** On polymerisation of these such compounds, networks are formed whose properties maybe selected depending upon the precise nature of the R^{11'} group, the amount of chain terminator present and the polymerisation conditions employed.

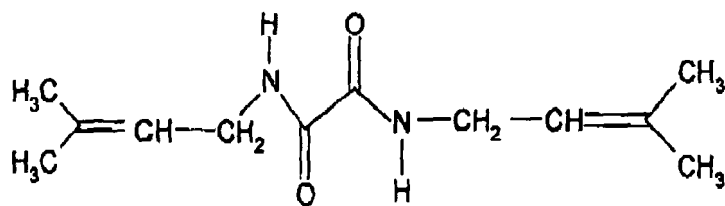
[0031] Examples of suitable bridging groups include those found in polyethylenes, polypropylenes, nylons, as listed in Table 1. Further examples of bridging groups can be found in WO 00/06610.

Table 1

40

Polymer Type	Repeat Unit of Bridging Group
Polyethylene	CH ₂
Polystyrene	CH ₂ CH(C ₆ H ₅) where the phenyl ring is optionally substituted
Polyisobutylene	CH ₂ CH(CH(CH ₃) ₂)
Polyisoprene	CH ₂ CH(CH ₃)
Polytetrafluoroethylene	CH ₂ (CF ₂) _x CH ₂
Polyvinylidene fluoride	CH ₂ (CF ₂ CH ₂) _x
Polyethyleneoxide	(OCH ₂ CH(CH ₃)) _x O
Nylon	CH ₂ (NHCOCH ₂) _x CH ₂
Peptide	CH ₂ (NHCOCH _R) _x CH ₂
Polyurethanes	-NH-CO-O-

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(IX)

[0036] Composites may also be produced by polymerising compounds of formula (XIII) in the presence of other moieties such as graphite, ethers such as crown ethers or thioethers, phthalocyanines, bipyridyls or liquid crystal compounds, all of which will produce composite polymers with modified properties.

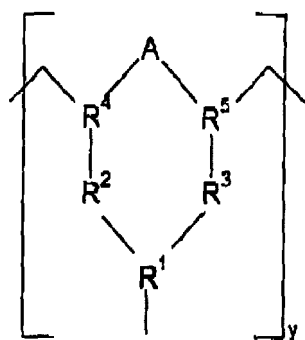
[0037] Using the method of the invention, it is possible to take a suitable organic system that has optimal or optimised properties for use in certain applications, e.g. high yield strength, large hyperpolarisability, high pyroelectric coefficient, high conductivity etc; and to structurally modify the system, so that it is possible to polymerise it. If functional groups are incorporated that will polymerise, it will become possible to create a three dimensional network or plastic that will have properties associated with the parent organic system.

[0038] The advantages of the compounds of the invention is that they allow for the possibility that they can be applied in the form of a paint and caused to polymerise in situ. This allows for ease of processing. Further, by providing for the construction of networks as a result of the cross linking, the resultant polymer can be mechanically strong and durable.

[0039] The starting material may be applied to a substrate prior to polymerisation and the polymerisation results in the production of a coating on the substrate.

[0040] According to a second aspect of the invention there is provided a polymer obtained by a method in accordance with the first aspect of the invention.

[0041] The polymer may be of sub-formula (VII)

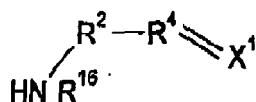


(VII)

where A is a bond or CY^2Y^3 , R^1 , R^2 , R^3 , R^4 , R^5 , R^{16} , CX^2X^3 and CY^2Y^3 are as defined in relation to sub-formula (XIII), and y is an integer in excess of 1, preferably in excess of 5.

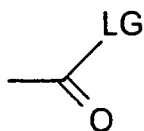
[0042] According to a third aspect of the invention there is provided a monomeric compound which includes a group of sub-formula (XIII) as defined in the first aspect of the invention. The monomer may include any group or consist of any compound described in accordance with the first aspect of the invention.

[0043] According to another aspect of the invention there is provided a method of preparing a monomeric compound in accordance with the third aspect of the invention including the step of reacting a compound having a group of sub-formula (XI)



(XI)

with a compound having a group of sub-formula (XII)



(XII)

where X¹, Y¹, R¹, R², R³, R⁴, R⁵ and R⁶ are as defined in the first aspect of the invention, and LG is a leaving group.

[0044] LG may be a halogen, with chloro being particularly preferred. Alternatively, LG may be mesylate, silyl or tosylate. The reaction may be effected in an organic solvent, such as acetone. Compounds of formulae (XI) and (XII) are either known compounds or can be prepared by conventional methods.

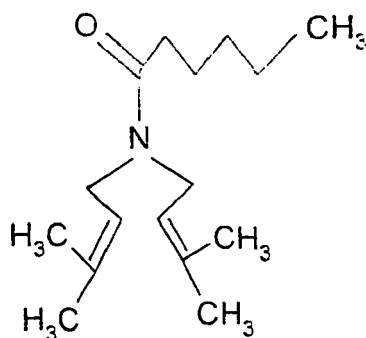
[0045] Embodiments of monomers, polymers, and methods for preparing same will now be described with reference to the accompanying drawings, in which:-

Figure 1 shows a first reaction scheme; and

Figure 2 shows a second reaction scheme.

Example 1

[0046] The target molecule 1 (hexanoic acid (bis(3-methylbut-2-enyl) amide) is shown below

1

and the synthetic scheme is shown in Figure 1.

[0047] The synthesis of monomer 1 is described below. Reactions 1.1, 1.2, 1.3 and 1.4 were carried out under an atmosphere of argon using pre-dried solvents; t-butyl methyl ether was dried over CaSO₄ overnight, passed through alumina and fractionally distilled, pyridine was dried over Linde type 4A molecular sieves followed by distillation, tetrahydrofuran (THF) was refluxed over sodium-benzophenone mixture before collection.

[0048] Column chromatography was carried out using flash grade silica.

1.1 Synthesis of 1-bromo-3-methylbut-2-ene(2)

[0049] t-Butyl methyl ether (1000 ml) and 3-methylbuten-3-ol (230g, 280ml, 2.67 moles) were charged into a multi neck flung flask (3 L) fitted with a mechanical stirrer, condenser, thermometer and a dropping funnel. Pyridine (21g, 22ml, 0.267 moles) was added and the contents of the flask were stirred at room temperature for 30 minutes after which time PBr₃ (361g, 125ml, 1.33 moles) was added with stirring via dropping funnel at such a rate as to maintain the internal temperature below 40°C, preferably around 30°C (note that the reaction is exothermic). Once addition was complete the reaction mixture was allowed to stir for 4 hours. After this time TLC and HPLC indicated that the reaction had gone to completion. Once at room temperature, the mixture was quenched by the addition of saturated NaCl solution with stirring (1 L).

[0050] The organic layer was separated and aqueous layer extracted with t-butyl methyl ether (3 x 300ml). Combined organic layers were washed twice with saturated NaHCO₃ (2x 500ml) followed by water (2x 200ml) then with brine (500ml). The ether layer was dried over anhydrous MgSO₄ and solvent removed under atmospheric pressure. The distillation apparatus was connected to a vacuum pump (water pump) and the bromide was distilled at 40 - 60 degrees at pressure of about 25 mmHg to afford a pale yellow oil (318g, 80% yield).

1.2 Preparation of Tertiary amine (3)

5 [0051] A multi neck flung flask (2L), fitted with a mechanical stirrer, condenser, thermometer and dropping funnel, and placed in a cooling bath (ice-water) was charged with acetone (500ml), concentrated aqueous ammonia solution (30 ml) and anhydrous potassium carbonate (159g, 1.15 mole). The mixture was stirred at room temperature for 30 minutes. Allyl bromide (52.5g, 0.35 mole) was added via a dropping funnel at such a rate that the internal reaction is maintained below 25 degrees for 20 minutes. The reaction was stirred at room temperature for 3 hours after which time TLC (silica, 5% methanol in DCM) indicated reaction completion. The solid suspension was filtered off and washed with acetone (2x50 ml). The solvent was evaporated under reduced pressure and the tertiary amine 3 was obtained as a pale yellow which solidified on standing (28g, 107% crude).

1.3 Preparation of Secondary Amine (4)

15 [0052] Crude tertiary amine (9g, 41 mmol) was placed in a 25 ml round bottomed (RB) flask fitted with a condenser. The contents of the flask were heated in a DrySyn (RTM) (an aluminium block) placed on a stirrer hot plate to 200°C (external temperature) over 30 minutes. Solid material started to melt at around 140 - 150°C. The material was heated at 200°C for 2.5 hours. The progress of the reaction was monitored by TLC (silica, 10% methanol in DCM with 5 drops of methanolic ammonia solution). After this time the reaction mixture was allowed to cool to room temperature.

20 1.4 Preparation of hexanoic acid (bis (3-methylbut-2-enyl) amide

25 [0053] The cool reaction mixture from the previous step was transferred to a 100ml RB flask containing potassium carbonate (6g, 43 mmole) with 30ml acetone. This was stirred at room temperature and hexanoyl chloride (3.8g, 3ml, 28 mmole) was added dropwise via a dropping funnel over 10 minutes with stirring. The reaction mixture was allowed to stir at room temperature overnight, and the next day TLC (silica plates, 2.5% methanol in DCM) indicated the formation of the target monomer 1. The solvent was removed under reduced pressure and solids were washed with 30 ml of petroleum ether (40 - 60) and filtered. Decolorising charcoal (1g) was added to the filtrate and heated to boil and then filtered hot. Solvent was removed under reduced pressure to afford a pale brown oil (5.0g, 49% yield). HPLC indicated a purity of 94%.

30 Example 2**Polymerisation of hexanoic acid (bis (3-methylbut-2-enyl) amide (1)**

35 [0054] Hexanoic acid (bis (3-methylbut-2-enyl) amide 1 polymerised easily under UV radiation (mercury discharge UV emitter) using ca 1.5% by weight of Irgacure 184 photoinitiator. Exposure times as little as 1 second were sufficient to effect polymerisation. The polymer produced thereby was extremely resistant to solvents.

40 Example 3**Polymerisation of hexanoic acid (bis (3-methylbut-2-enyl) amide (1) without photoinitiator**

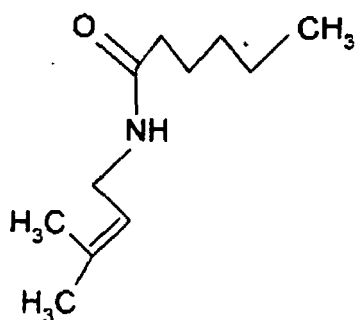
45 [0055] Hexanoic acid (bis (3-methylbut-2-enyl) amide 1 polymerised under UV radiation (mercury discharge UV emitter) without employing a photoinitiator. Cure was effected in as little as 1 second. Polymerisation was equally facile in a further experiment using LED UV light sources operating at 390 nm to cure the monomer in the absence of photoinitiator.

Example 4

50 [0056] The target molecule 5 (hexanoic acid (3-methylbut-2-enyl) amide) is shown below

5

10

5

and the synthetic scheme is shown in Figure 2.

15

4.1 Synthesis of 1-bromo-3-methylbut-2-ene (6)

20

[0057] 3-methyl-but-3-en-2-ol (97%, 500ml) was added to hydrobromic acid (48%, 1 L) at room temperature with constant stirring for 2 hours. The mixture was then left to stand for another 2 hours, after which the top transparent yellow layer was decanted away from the aqueous/HBr bottom layer. The top layer was dried thoroughly over CaSO₄ and then distilled at 63°C to produce a colourless liquid of density 1.26 g/ml.

4.2 Preparation of Primary Amine (7)

25

[0058] The bromo methyl butane 6 was dissolved in acetone (50ml) and this solution added dropwise, with stirring, to a pre-cooled solution to -5°C of concentrated aqueous ammonium hydroxide (25ml) in the presence of potassium carbonate (22g). The mixture was stirred at this temperature for 30 minutes after which time it was allowed to come to room temperature. The solvent and primary amine 7 were removed in-vacuo.

4.3 Preparation of hexanoic acid (3-methylbut-2-enyl) amide (5)

30

[0059] Hexanoyl chloride (3.8g) was added dropwise to the secondary amine and acetone, with stirring, over 30 minutes at room temperature. The reaction was allowed to stir for four hours after which time the solvent was removed in-vacuo to leave a yellow oil, which was purified by silica gel flash column chromatography using dichloromethane as eluent. The target monomer 5 is a pale yellow oil.

35

Example 5

Polymerisation of hexanoic acid (3-methylbut-2-enyl) amide (5)

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[0060] The monomer 5 polymerised under UV radiation using the conditions described in Example 2.

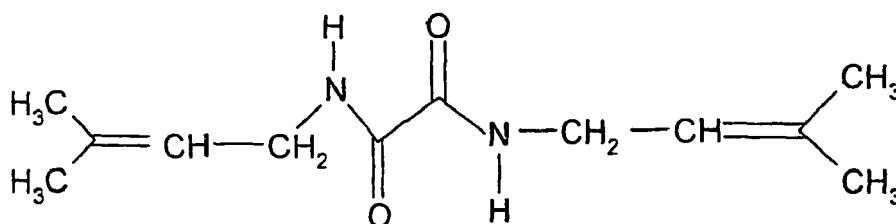
Example 6

Polymerisation of hexanoic acid (3-methylbut-2-enyl) amide (5) with a cross-linker

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[0061] Monomer 5 was produced in accordance with Example 4, and was copolymerised with a cross-linker compound

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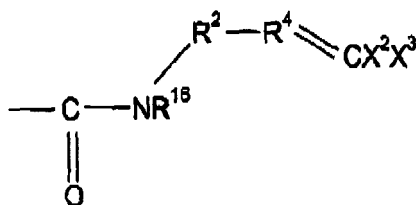
[0062] The cross-linker compound was prepared using the methodology described in Example 4, with the exception that the hexanoyl chloride used in step 4.3 was replaced with oxaloyl chloride (ClOCCOCl) in a molar ratio of 2:1

(primary amine 7: oxaloyl chloride). The cross-linker (5%) was dissolved in monomer 5 (95%) at room temperature, and the resultant solution copolymerised easily using polymerisation conditions as described in Example 2.

5 **Claims**

1. A method of producing a polymeric material, said method including the step of subjecting a starting material which includes a group of sub-formula (XIII)

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(XIII)

15

20

where R¹⁰ is selected from hydrogen, halo, nitro, hydrocarbyl, optionally substituted or interposed with functional groups, or -R³-R⁵=CY²Y³;

R² and R³ are independently selected from (CR⁶R⁷)_n or a group CR⁸CR⁶R⁷CR⁸R⁹ or CR⁸R⁹CR⁶R⁷ where n is 0, 1 or 2, R⁶ and R⁷ are independently selected from hydrogen or alkyl, and either one of R⁸ or R⁹ is hydrogen and the other is an electron withdrawing group, or R⁸ or R⁹ together form an electron withdrawing group; and

25

R⁴ and R⁵ are independently selected from CH or CR¹⁰ where CR¹⁰ is an electron withdrawing group,

and X² and X³, and, if present, Y² and Y³, are each a C₁ to C₄ alkyl group;

to conditions under which polymerisation of the starting material occurs.

30

2. A method according to claim 1 in which X², X³, Y² and Y³ are each either methyl or ethyl.

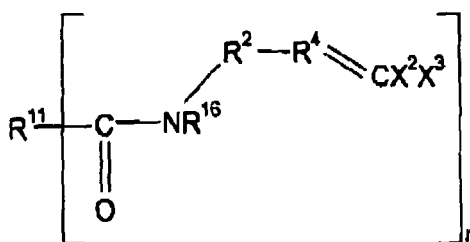
3. A method according to claim 2 in which X², X³, Y² and Y³ are each methyl.

4. A method according to any previous claim in which the group of sub-formula (XIII) includes the group -R³-R⁵=CY²Y³, the polymerisation of the starting material is a cyclopolymerisation reaction, and at least one of (a) R² and R³ or (b) R⁴ and R⁵ includes an electron withdrawing group which is able to activate a cyclopolymerisation reaction.

35

5. A method according to any one of the preceding claims wherein the starting material is a compound of structure (XIV)

40



(XIV)

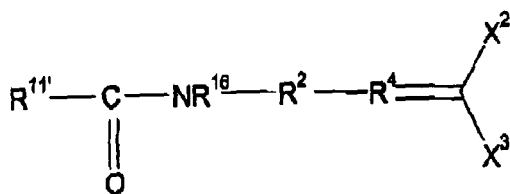
45

where R², R⁴, R¹⁶, X² and X³ are as defined in claim 1, r is an integer of 1 or more, and R¹¹ is a bridging group, an optionally substituted hydrocarbyl group, a perhaloalkyl group, a siloxane group or an amide, of valency r.

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6. A method according to claim 5 wherein the starting material - comprises a compound of formula (XV)

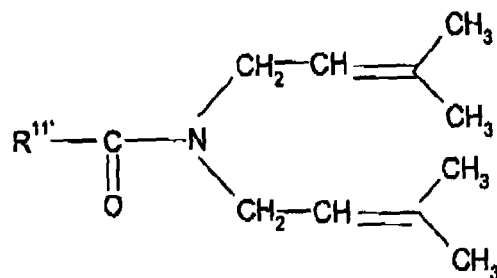
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(XV)

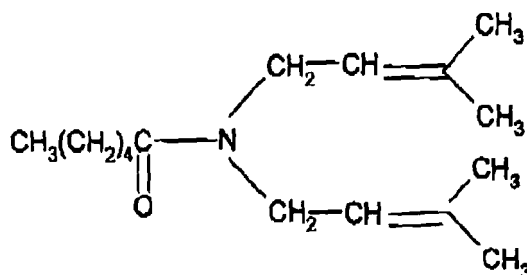
and where X^2 , X^3 , Y^2 , Y^3 , R^2 , R^3 , R^4 , R^5 , and R^{16} are as defined in claim 1, and $R^{11'}$ is an optionally substituted hydrocarbyl group, a perhaloalkyl group, a siloxane group or an amide.

7. A method according to claim 5 or claim 6 in which R^{11} or $R^{11'}$ comprises a straight or branched chain hydrocarbyl group, optionally substituted or interposed with functional groups.
8. A method according to claim 7 in which R^{11} or $R^{11'}$ is an optionally substituted hydrocarbyl group having four or more carbon atoms.
9. A method according to claim 8 in which R^{11} or $R^{11'}$ is a straight or branched chain alkyl group having four or more carbon atoms.
10. A method according to any one of claims 6 to 9 wherein the compound of formula (XV) is a compound of formula (IV)



(IV)

11. A method according to claim 10 in which the compound of formula (IV) is a compound of formula (V)



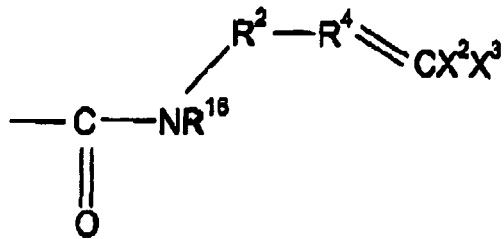
(V)

12. A polymer obtained by a method according to any one of claims 1 to 11.
13. A monomeric compound which includes a group of sub-formula (XIII) as defined in claim 1.

Patentansprüche

1. Verfahren zur Herstellung eines polymeren Materials, wobei das Verfahren den Schritt des Aussetzens eines Ausgangsmaterials, das eine Gruppe der Teilformel (XIII)

5



(XIII)

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umfasst, worin

R¹⁶ aus Wasserstoff, Halogen, Nitro, Hydrocarbyl, das gegebenenfalls mit funktionellen Gruppen substituiert ist oder eingefügte funktionelle Gruppen aufweist, oder -R³-R⁵=CY²Y³ ausgewählt ist,

R² und R³ unabhängig aus (CR⁶R⁷)_n oder einer Gruppe CR⁸R⁹, CR⁶R⁷CR⁸R⁹ oder CR⁸R⁹CR⁶R⁷ ausgewählt sind,

15

worin n 0, 1 oder 2 ist, R⁶ und R⁷ unabhängig aus Wasserstoff oder Alkyl ausgewählt sind und einer von R⁸ oder R⁹ Wasserstoff und der andere eine elektronenziehende Gruppe ist, oder R⁸ oder R⁹ zusammen eine elektronenziehende Gruppe bilden, und

R⁴ und R⁵ unabhängig aus CH oder CR¹⁰ ausgewählt sind, worin CR¹⁰ eine elektronenziehende Gruppe ist,

und X² und X³ und, falls vorhanden, Y² und Y³, jeweils eine C₁- bis C₄-Alkylgruppe sind,

gegenüber Bedingungen umfasst, bei denen eine Polymerisation des Ausgangsmaterials stattfindet.

20

2. Verfahren nach Anspruch 1, bei dem X², X³, Y² und Y³ jeweils entweder Methyl oder Ethyl sind.

3. Verfahren nach Anspruch 2, bei dem X², X³, Y² und Y³ jeweils Methyl sind.

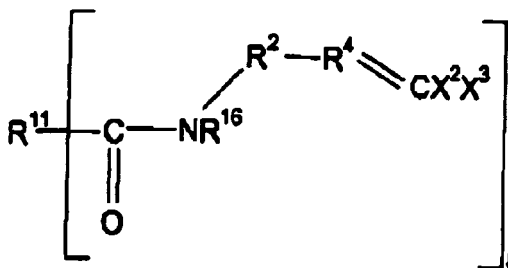
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4. Verfahren nach einem der vorhergehenden Ansprüche, bei dem die Gruppe der Teilformel (XIII) die Gruppe -R³-R⁵=CY²Y³ umfasst, die Polymerisation des Ausgangsmaterials eine Cyclopolymerisationsreaktion ist und mindestens einer von (a) R² und R³ und (b) R⁴ und R⁵ eine elektronenziehende Gruppe umfasst, die eine Cyclopolymerisationsreaktion aktivieren kann.

30

5. Verfahren nach einem der vorhergehenden Ansprüche, bei dem das Ausgangsmaterial eine Verbindung der Struktur (XIV)

35



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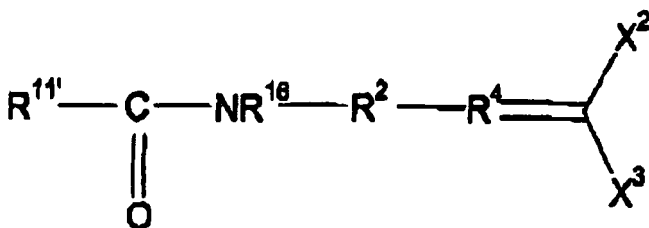
(XIV)

45

ist, worin R², R⁴, R¹⁶, X² und X³ wie in Anspruch 1 definiert sind, r eine ganze Zahl von 1 oder mehr ist und R¹¹ eine verbrückende Gruppe, eine gegebenenfalls substituierte Hydrocarbylgruppe, eine Perhalogenalkylgruppe, eine Siloxangruppe oder ein Amid mit der Wertigkeit r ist.

6. Verfahren nach Anspruch 5, bei dem das Ausgangsmaterial eine Verbindung der Formel (XV)

50

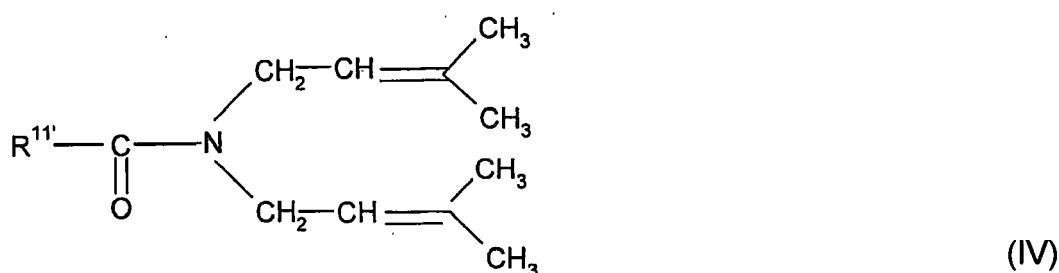


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(XV)

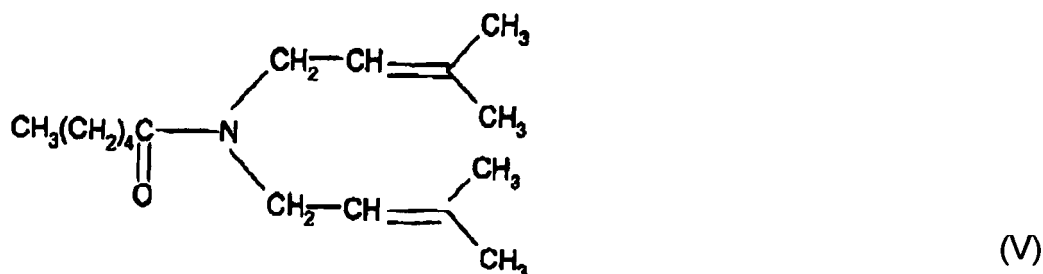
umfasst und wobei $X^2, X^3, Y^2, Y^3, R^2, R^3, R^4, R^5$ und R^{16} wie im Anspruch 1 definiert sind und $R^{11'}$ eine gegebenenfalls substituierte Hydrocarbylgruppe, eine Perhalogenalkylgruppe, eine Siloxangruppe oder ein Amid ist.

- 5 7. Verfahren nach Anspruch 5 oder Anspruch 6, bei dem R^{11} oder $R^{11'}$ eine geradkettige oder verzweigte Hydrocarbylgruppe umfasst, die gegebenenfalls mit funktionellen Gruppen substituiert ist oder eingefügte funktionelle Gruppen aufweist.
- 10 8. Verfahren nach Anspruch 7, bei dem R^{11} oder $R^{11'}$ eine gegebenenfalls substituierte Hydrocarbylgruppe mit vier oder mehr Kohlenstoffatomen ist.
9. Verfahren nach Anspruch 8, bei dem R^{11} oder $R^{11'}$ eine geradkettige oder verzweigte Alkylgruppe mit vier oder mehr Kohlenstoffatomen ist.
- 15 10. Verfahren nach einem der Ansprüche 6 bis 9, bei dem die Verbindung der Formel (XV) eine Verbindung der Formel (IV)



ist.

- 30 11. Verfahren nach Anspruch 10, bei dem die Verbindung der Formel (IV) eine Verbindung der Formel (V)



ist.

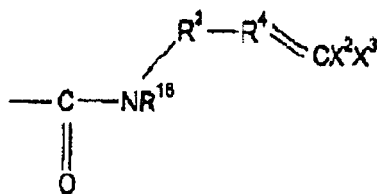
- 45 12. Polymer, erhalten durch ein Verfahren nach einem der Ansprüche 1 bis 11.
13. Monomere Verbindung, die eine Gruppe der Teilformel (XIII), wie sie im Anspruch 1 definiert ist, umfasst.

50 **Revendications**

1. Procédé de production d'une matière polymérique, ledit procédé comprenant l'étape consistant à soumettre une matière de départ qui comprend un groupe de sous-formule (XIII)

55

5



(XIII)

10 où R¹⁶ est choisi parmi un atome d'hydrogène, un groupe halogéno, nitro, hydrocarbyle, facultativement substitué ou interposé avec des groupes fonctionnels, ou -R³-R⁵=CY²Y³ ;

R² et R³ sont indépendamment choisis parmi (CR⁶R⁷)_n ou un groupe CR⁸R⁹, CR⁶R⁷CR⁸R⁹ ou CR⁸R⁹CR⁶R⁷, où n vaut 0, 1 ou 2, R⁶ et R⁷ sont indépendamment choisis parmi un atome d'hydrogène ou un groupe alkyle, et soit l'un parmi R⁸ et R⁹ est un atome d'hydrogène et l'autre est un groupe électroattracteur, ou R⁸ et R⁹ forment ensemble

15 un groupe électroattracteur ; et

R⁴ et R⁵ sont indépendamment choisis parmi CH ou CR¹⁰, où CR¹⁰ est un groupe électroattracteur, et X² et X³, et, s'ils sont présents, Y² et Y³, sont chacun un groupe alkyle en C₁ à C₄ ; à des conditions dans lesquelles la polymérisation de la matière de départ se produit.

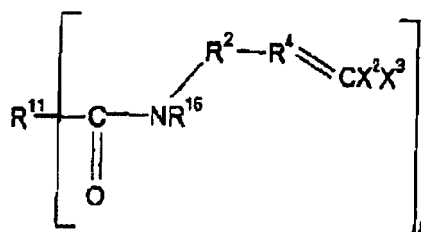
20 2. Procédé selon la revendication 1, dans lequel X², X³, Y² et Y³ sont chacun soit un groupe méthyle, soit un groupe éthyle.

3. Procédé selon la revendication 2, dans lequel X², X³, Y² et Y³ sont chacun un groupe méthyle.

25 4. Procédé selon l'une quelconque des revendications précédentes, dans lequel le groupe de R³-R⁹=CY²Y³ sous-formule (XIII) comprend le groupe la polymérisation de la matière de départ est une réaction de cyclopolymérisation, et au moins l'un de (a) R² et R³ ou (b) R⁴ et R⁵ comprend un groupe électroattracteur qui est capable d'activer une réaction de cyclopolymérisation.

30 5. Procédé selon l'une quelconque des revendications précédentes, dans lequel la matière de départ est un composé de structure (XIV)

35



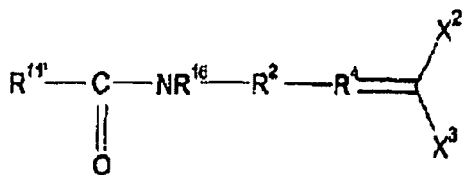
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(XIV)

45 où R², R⁴, R¹⁶, X² et X³ sont tels que définis dans la revendication 1, r est un nombre entier de 1 ou plus, et R¹¹ est un groupe de pontage, un groupe hydrocarbyle facultativement substitué, un groupe perhalogénoalkyle, un groupe siloxane ou un amide, de valence r.

6. Procédé selon la revendication 5, dans lequel la matière de départ comprend un composé de formule (XV)

50



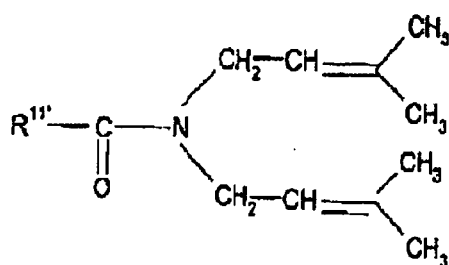
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(XV)

et où X², X³, Y², Y³, R², R³, R⁴, R⁵ et R¹⁶ sont tels que définis dans la revendication 1, et R¹¹ est un groupe hydrocarbyle facultativement substitué, un groupe perhalogénoalkyle, un groupe siloxane ou

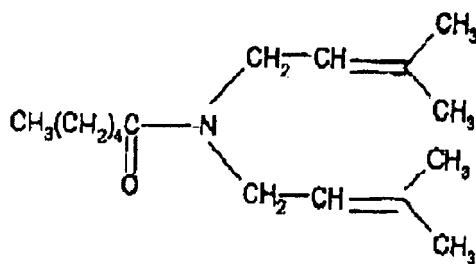
un amide.

7. Procédé selon la revendication 5 ou la revendication 6, dans lequel R¹¹ ou R^{11'} comprend un groupe hydrocarbyle à chaîne droite ou ramifiée, facultativement substitué ou interposé avec des groupes fonctionnels.
8. Procédé selon la revendication 7, dans lequel R¹¹ ou R^{11'} est un groupe hydrocarbyle facultativement substitué comportant quatre atomes de carbone ou plus.
9. Procédé selon la revendication 8, dans lequel R¹¹ ou R^{11'} est un groupe alkyle à chaîne droite ou ramifiée comportant quatre atomes de carbone ou plus.
10. Procédé selon l'une quelconque des revendications 6 à 9, dans lequel le composé de formule (XV) est un composé de formule (IV)



(IV)

11. Procédé selon la revendication 10, dans lequel le composé de formule (IV) est un composé de formule (V)



(V)

12. Polymère obtenu par un procédé selon l'une quelconque des revendications 1 à 11.
13. Composé monomérique qui comprend un groupe de sous-formule (XIII) tel que défini dans la revendication 1.

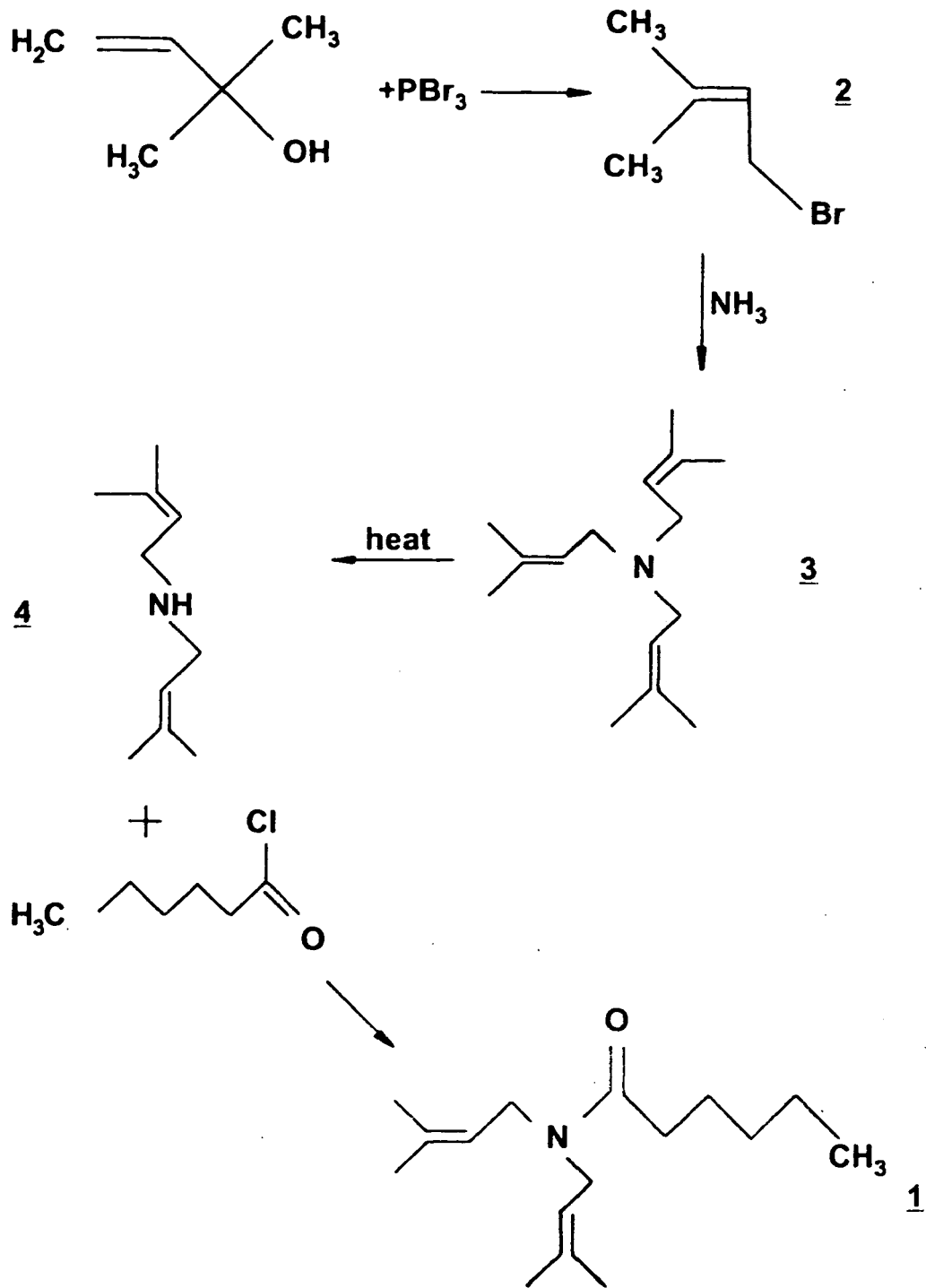


Fig. 1

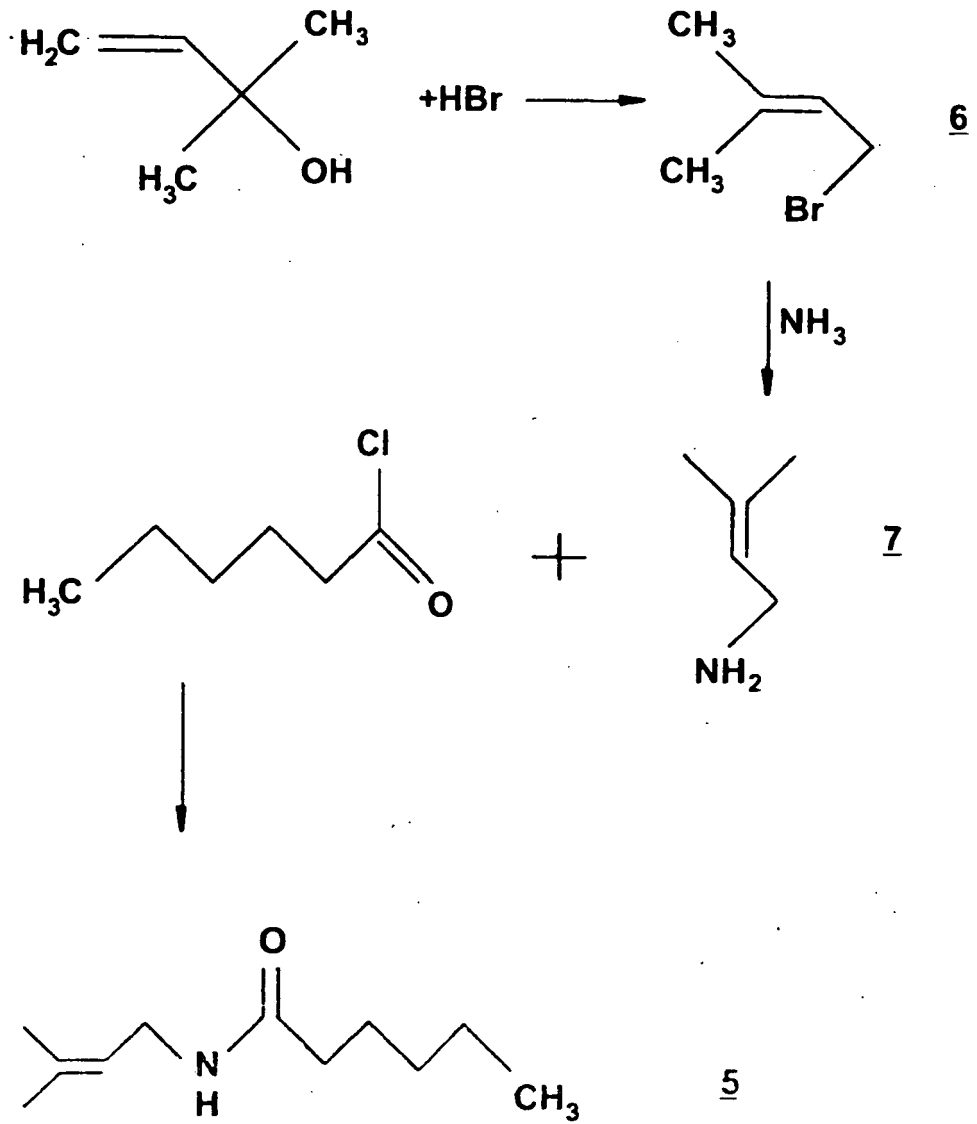


Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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