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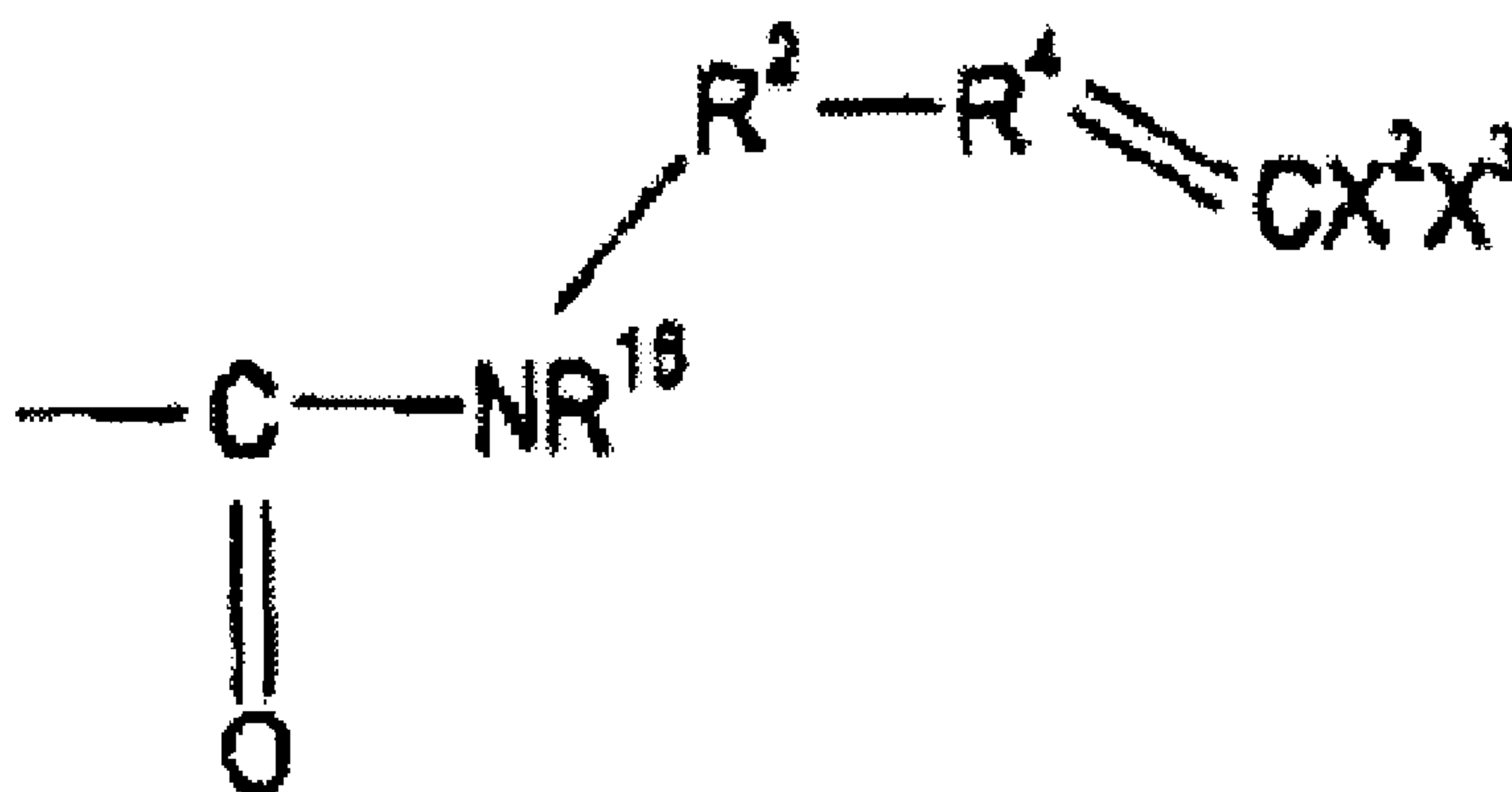
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(54) Titre : MATIERES POLYMERIQUES ET PROCEDES SERVANT A FABRIQUER CELLES-CI

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



(XIII)

(57) **Abrégé/Abstract:**

This invention relates to a method of producing a polymeric material, said method including the step of subjecting a starting material which includes a group of sub-formula (I): where R^1 is CR^aR^b , where R^b is hydrogen or alkyl and R^a is hydrogen, alkyl or $-R^3 - R^5 \equiv Y^1$, or R is an electron withdrawing group, R^2 and R^3 are independently selected from $(CR^{6R^{77}})_n$ or a group CR^8R^9 , $CR^6R^7CR^8R^9$ or $CR^8R^9CR^6R^7$ 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 CH or CR^{10} where CR^{10} is an electron withdrawing group, the dotted lines indicate the presence or absence of a bond, X^1 is a group CX^2X^3 where the dotted line bond to which it is attached is absent and a group CX^2 where the dotted line bond to which it is attached is present, Y^1 is a group CY^2Y^3 where the dotted line bond to which it is attached is absent and a group CY^2 where the dotted line bond to which it is attached is present, and at least one of, and preferably all of, X^2 , X^3 , Y^2 and Y^3 are substituents other than hydrogen and fluorine; to conditions under which polymerisation of the starting material occurs, with the proviso that if R^1 is a group $N^+HR^{16}(Zm^-)_{1/m}$, where R^{16} is selected from hydrogen, hydrocarbonyl or $-R^3 - R^5 \equiv Y^1$ only, and Z is an anion of charge m ; then either (i) the polymerisation is a homopolymerisation or a copolymerisation in which the anion Z does not form a repeat unit in a resulting polymeric chain, or (ii) the starting material only includes one group of formula $-R^2$

(57) Abrégé(suite)/Abstract(continued):
- $R^4 \equiv X^1$

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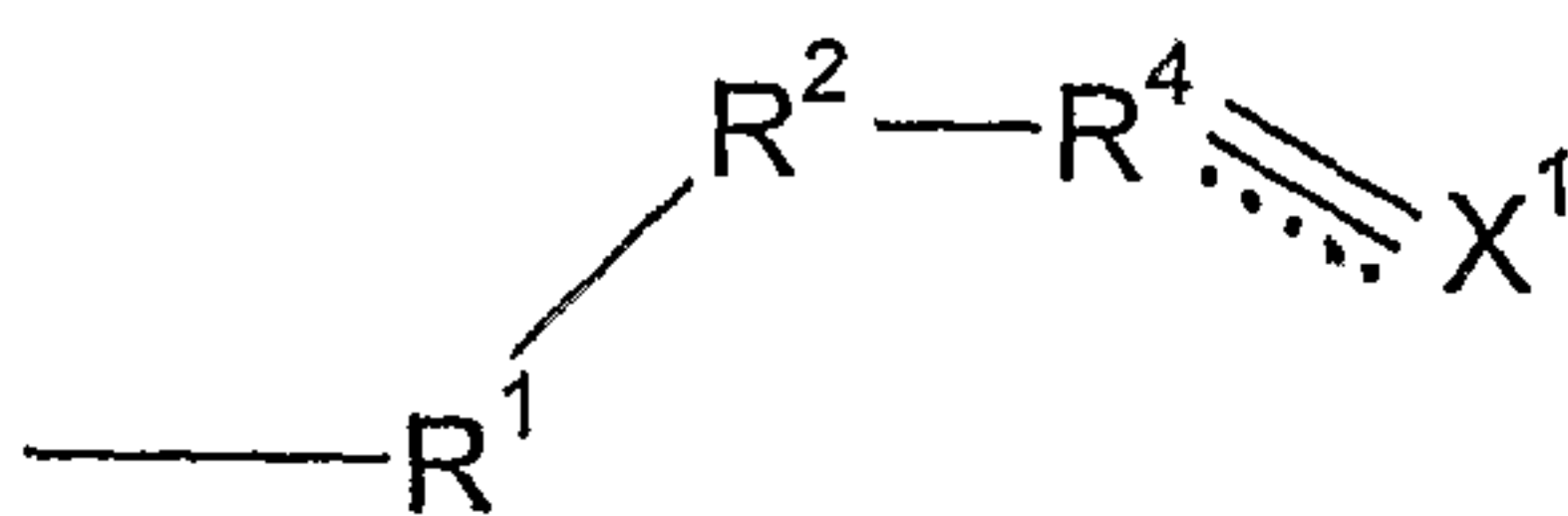
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(54) Title: METHOD OF PRODUCING A POLYMERIC MATERIAL, POLYMER, MONOMERIC COMPOUND AND METHOD OF PREPARING A MONOMERIC COMPOUND



(I)

(57) Abstract: This invention relates to a method of producing a polymeric material, said method including the step of subjecting a starting material which includes a group of sub-formula (I): where R^1 is CR^aR^b , where R^b is hydrogen or alkyl and R^a is hydrogen, alkyl or $-\text{R}^3 - \text{R}^5 \equiv \text{Y}^1$, or R is an electron withdrawing group, R^2 and R^3 are independently selected from $(\text{CR}^6\text{R}^7)_n$ or a group CR^8R^9 , $\text{CR}^6\text{R}^7\text{CR}^8\text{R}^9$ or $\text{CR}^8\text{R}^9\text{CR}^6\text{R}^7$ 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 CH or CR^{10} where CR^{10} is an electron withdrawing group, the dotted lines indicate the presence or absence of a bond, X^1 is a group CX^2X^3 where the dotted line bond to which it is attached is absent and a group CX^2 where the dotted line bond to which it is attached is present, Y^1 is a group CY^2Y^3 where the dotted line bond to which it is attached is absent and a group CY^2 where the dotted line bond to which it is attached is present, and at least one of, and preferably all of, X^2 , X^3 , Y^2 and Y^3 are substituents other than hydrogen and fluorine; to conditions under which polymerisation of the starting material occurs, with the proviso that if R^1 is a group $\text{N}^+\text{HR}^{16}(\text{Z}^{m-})_{1/m}$, where R^{16} is selected from hydrogen, hydrocarbonyl or $-\text{R}^3 - \text{R}^5 \equiv \text{Y}^1$ only, and Z is an anion of charge m; then either (i) the polymerisation is a homopolymerisation or a copolymerisation in which the anion Z does not form a repeat unit in a resulting polymeric chain, or (ii) the starting material only includes one group of formula $-\text{R}^2 - \text{R}^4 \equiv \text{X}^1$

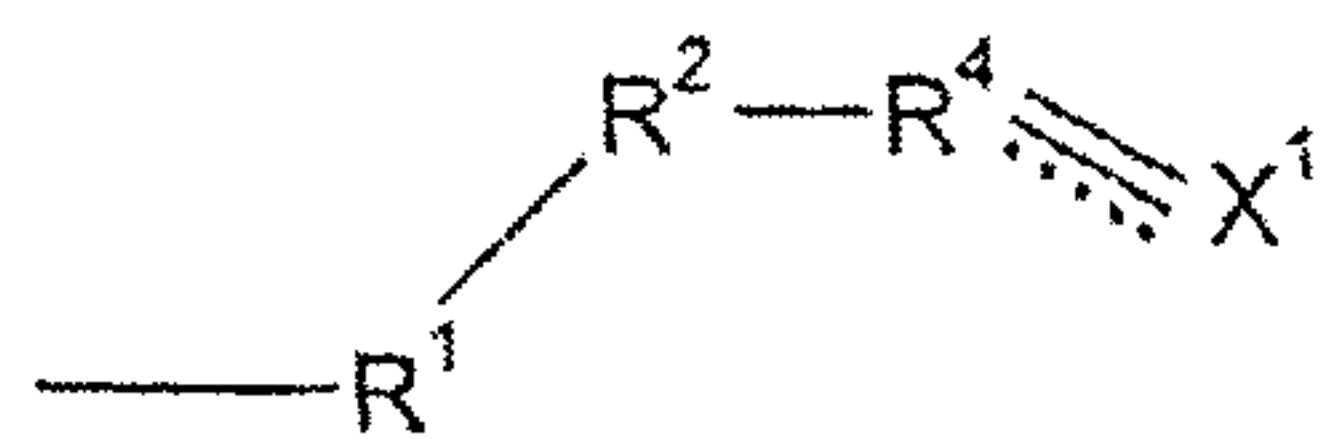
WO 2008/001102 A1

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

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

International Publications WO 00/06610, WO 00/06533, WO 00/06658, WO 01/36510, WO 01/40874 and WO 01/74919 disclose 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.

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 (I)



(I)

where R^1 is CR^aR^b , where R^a is hydrogen or alkyl and R^b is hydrogen, alkyl or $\text{---}R^3\text{---}R^5\text{---}Y^1$, or R^1 is an electron withdrawing group,

5 R^2 and R^3 are independently selected from $(CR^6R^7)_n$ or a group CR^8R^9 , $CR^6R^7CR^8R^9$ or $CR^8R^9CR^6R^7$ 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

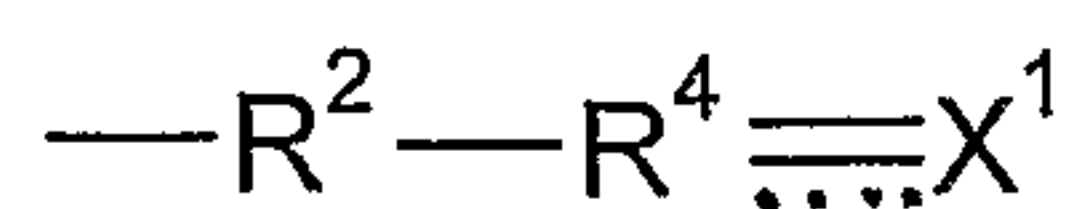
10 R^4 and R^5 are independently selected from CH or CR^{10} where CR^{10} is an electron withdrawing group,

the dotted lines indicate the presence or absence of a bond, X^1 is a group CX^2X^3 where the dotted line bond to which it is attached is absent and a group CX^2 where the dotted line bond to which it is attached is present, Y^1 is a group
15 CY^2Y^3 where the dotted line bond to which it is attached is absent and a group CY^2 where the dotted line bond to which it is attached is present, and at least one of, and preferably all of, X^2 , X^3 , Y^2 and Y^3 are substituents other than hydrogen and fluorine;

to conditions under which polymerisation of the starting material occurs,

20 with the proviso that if R^1 is a group $N^+HR^{16}(Z^{m-})_{1/m}$, where R^{16} is selected from hydrogen, hydrocarbyl or $\text{---}R^3\text{---}R^5\text{---}Y^1$ only, and Z is an anion of charge m ; then either (i) the polymerisation is a homopolymerisation or a copolymerisation in which the anion Z does not form a repeat unit in a resulting

polymeric chain, or (ii) the starting material only includes one group of formula



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.

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 00/00610 can provide improved polymerisation. Without wishing to be bound by any particular theory, it is
5 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.

Polymers of the invention can be easily and conveniently polymerised, in
10 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.

Generally, at least one of, and preferably all of, X^2 , X^3 , Y^2 (when present) and Y^3 (when present) is a group or atom which can stabilise desired free radical
15 intermediates and/or destabilise unwanted free radical intermediates.

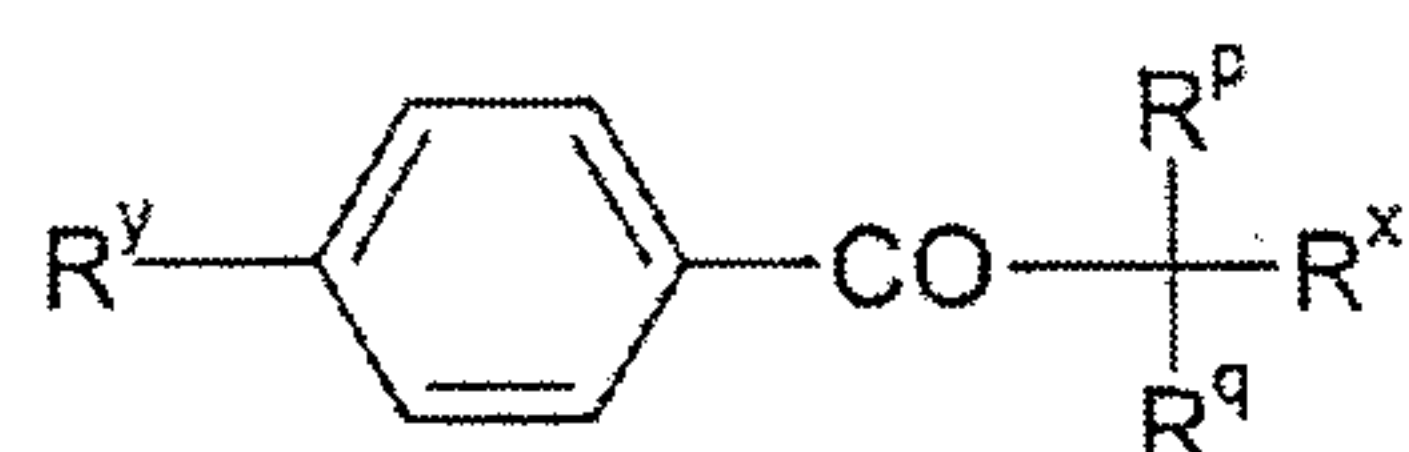
Preferably at least one, and most preferably all, of X^2 , X^3 , Y^2 and Y^3 is an optionally substituted hydrocarbyl group. Very preferably at least one, and most preferably all, of X^2 , X^3 , Y^2 and Y^3 is an optionally substituted alkyl group. Particularly preferred examples are C_1 to C_4 alkyl groups; especially methyl or
20 ethyl. Very surprisingly, it has been found that embodiments in which X^2 , X^3 , Y^2 and/or Y^3 are alkyl groups are able to polymerise on exposure to radiation without the presence of an initiator. Alternatively, at least one, and preferably all, of X^2 , X^3 , Y^2 and Y^3 are aryl and/or heterocyclic, such as pyridyl, pyrimidinyl, or a pyridine or pyrimidine containing group.

In one important range of embodiment, the group of the sub-formula (I) includes the group $\text{—R}^3\text{—R}^5\equiv\text{Y}^1$, 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.

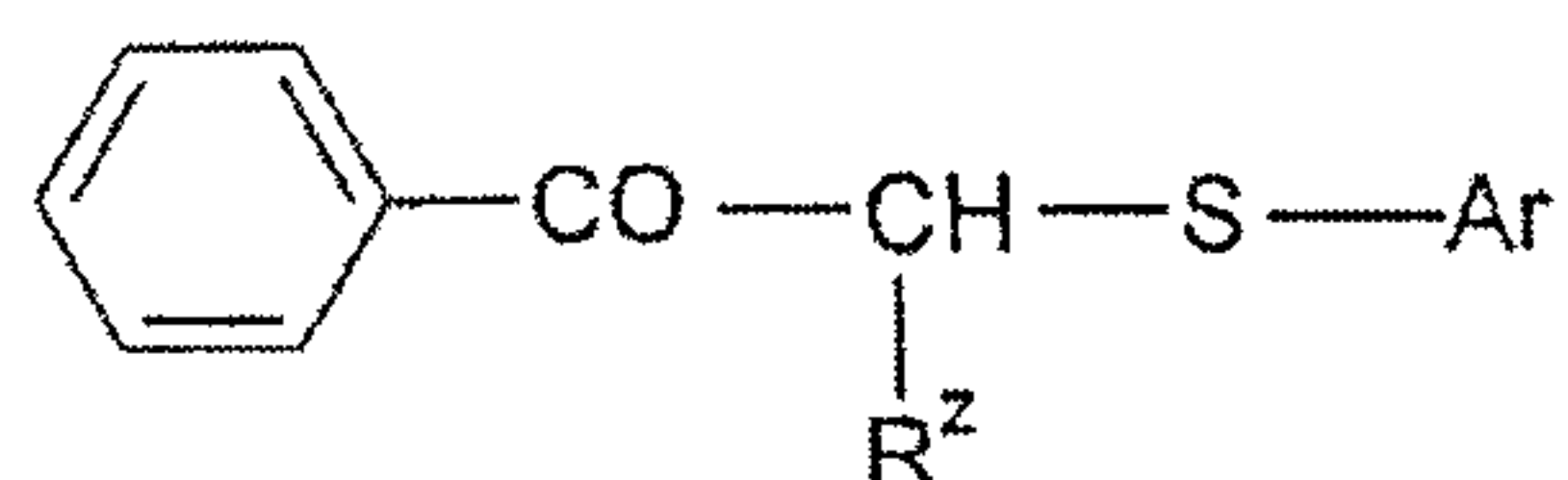
Conditions under which polymerisation occurs may comprise the application of radiation, such as UV radiation, where necessary in the presence of a photoinitiator (but preferably without an initiator present), the application of heat (which may be in form of IR radiation), where necessary in the presence 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.

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

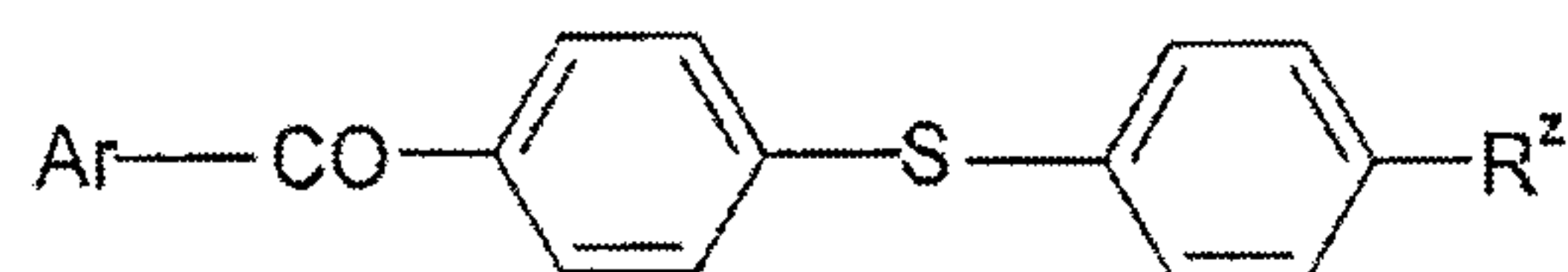
in particular acetophenone; chlorinated acetophenones such as di- or trichloracetophenone; dialkoxyacetophenones such as dimethoxyacetophenones (sold under the name Irgacure 651TM) dialkylhydroxyacetophenones such as
 5 dimethylhydroxyacetophenone (sold under the name Darocure 1173TM); substituted dialkylhydroxyacetophenone 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 names Darocure 1116TM and Trigonal P1TM); 1-
 10 benzoylcyclohexanol-2 (sold under the name Irgacure 184TM); 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 name Quantacure PDOTM); acylphosphine oxides, acylphosphonates such as
 15 dialkylacylphosphonate, ketosulphides 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-dialkyamino) 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 name Speedcure BMD5™).

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.

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, quinoliny, isoquinoliny, quinoxaliny, benzthiazolyl, benzoxazolyl, benzothienyl or benzofuryl.

The term "functional group" refers to reactive groups such as halo, cyano, nitro, oxo, $\text{C}(\text{O})_n\text{R}^e$, OR^e , $\text{S}(\text{O})_t\text{R}^e$, NR^fR^g , $\text{OC}(\text{O})\text{NR}^f\text{R}^g$, $\text{C}(\text{O})\text{NR}^f\text{R}^g$, $\text{OC}(\text{O})$

NR^fR^g , $-\text{NR}^7\text{C}(\text{O})_n\text{R}^6$, $-\text{NR}^e\text{CONR}^f\text{R}^g$, $-\text{C}=\text{NOR}^e$, $-\text{N}=\text{CR}^f\text{R}^g$, $\text{S}(\text{O})_t\text{NR}^f\text{R}^g$,
 $\text{C}(\text{S})_n\text{R}^e$, $\text{C}(\text{S})\text{OR}^e$, $\text{C}(\text{S})\text{NR}^f\text{R}^g$ or $-\text{NR}^f\text{S}(\text{O})_t\text{R}^e$ 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
5 further heteroatoms such as $\text{S}(\text{O})_s$, 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, $\text{C}(\text{O})_n\text{R}^e$, OR^e , $\text{S}(\text{O})_t\text{R}^e$, NR^fR^g , $\text{OC}(\text{O})\text{NR}^f\text{R}^g$,
 $\text{C}(\text{O})\text{NR}^f\text{R}^g$, $\text{OC}(\text{O})\text{NR}^f\text{R}^g$, $-\text{NR}^7\text{C}(\text{O})_n\text{R}^6$, $-\text{NR}^e\text{CONR}^f\text{R}^g$, $-\text{NR}^e\text{CSNR}^f\text{R}^g$,
 $\text{C}=\text{NOR}^e$, $-\text{N}=\text{CR}^f\text{R}^g$, $\text{S}(\text{O})_t\text{NR}^f\text{R}^g$, or $-\text{NR}^f\text{S}(\text{O})_t\text{R}^e$ where R^e , R^f and R^g , n and t
10 are as defined above.

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.

15 The term "amide" is generally understood to refer to a group of formula
 $\text{C}(\text{O})\text{NR}^e\text{R}^f$ 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 $\text{S}(\text{O})_2\text{NR}^e\text{R}^f$.

20 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.

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

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

Preferably, either i) R^1 is a group $N^+R^{12}R^{16}(Z^{m-})_{1/m}$,
 5 $S(O)_pR^{13}R^{16}$, BR^{16} , $P(O)_qR^{14}R^{16}$ or $Si(R^{15}R^{16})$ where R^{12} is hydrogen, halo, nitro or hydrocarbyl, optionally substituted or interposed with functional groups; R^{13} , R^{14} , and R^{15} are independently selected from hydrogen or hydrocarbyl; R^{16} is selected from hydrogen, halo, nitro, hydrocarbyl, optionally substituted or interposed with functional groups, or $-R^3-R^5\equiv Y^1$ where R^3 , R^5 and Y^1 are
 10 as defined previously; Z is an anion of charge m ; p is 0, 1, or 2; and q is 1 or 2; or ii) R^1 is $C(O)NR^{16-}$, $S(O)_2NR^{16-}$, $C(O)ONR^{16-}$, CH_2ONR^{16-} , or $CH=CHR^cNR^{16-}$ where R^c is an electron withdrawing group or iii) R^1 is $OC(O)CHR^{16-}$, $C(O)CHR^{16-}$ or $S(O)_2CHR^{16-}$.

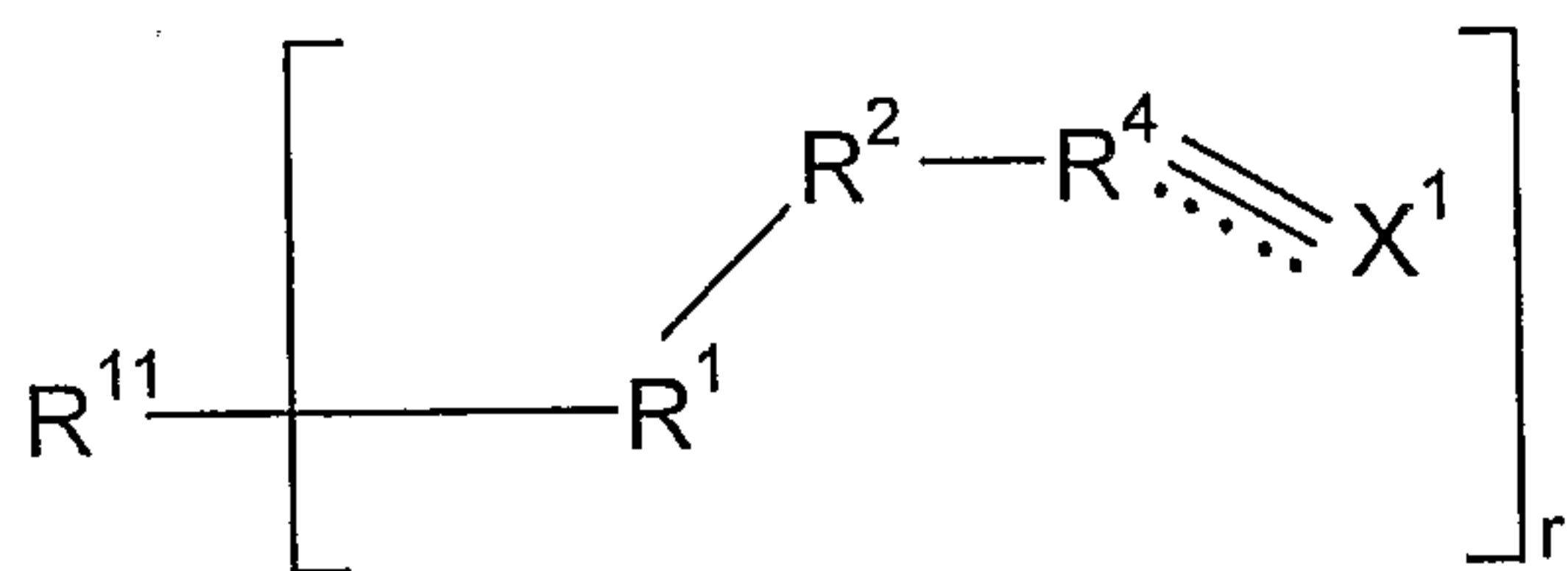
When R^1 is $N^+R^{12}R^{16}(Z^{m-})_{1/m}$, Z may be a halide ion, a boride ion, or a
 15 carboxylic acid ester.

When R^1 is $CH=CHR^dNR^{16-}$, R^d may be a carbonyl group or phenyl substituted at the ortho and/or para positions by an electron withdrawing substituent such as nitro.

In the group of sub-formula (1), X^1 and, where present, Y^1 preferably
 20 represents CX^2X^3 and CY^2Y^3 respectively, and the dotted bonds are absent.

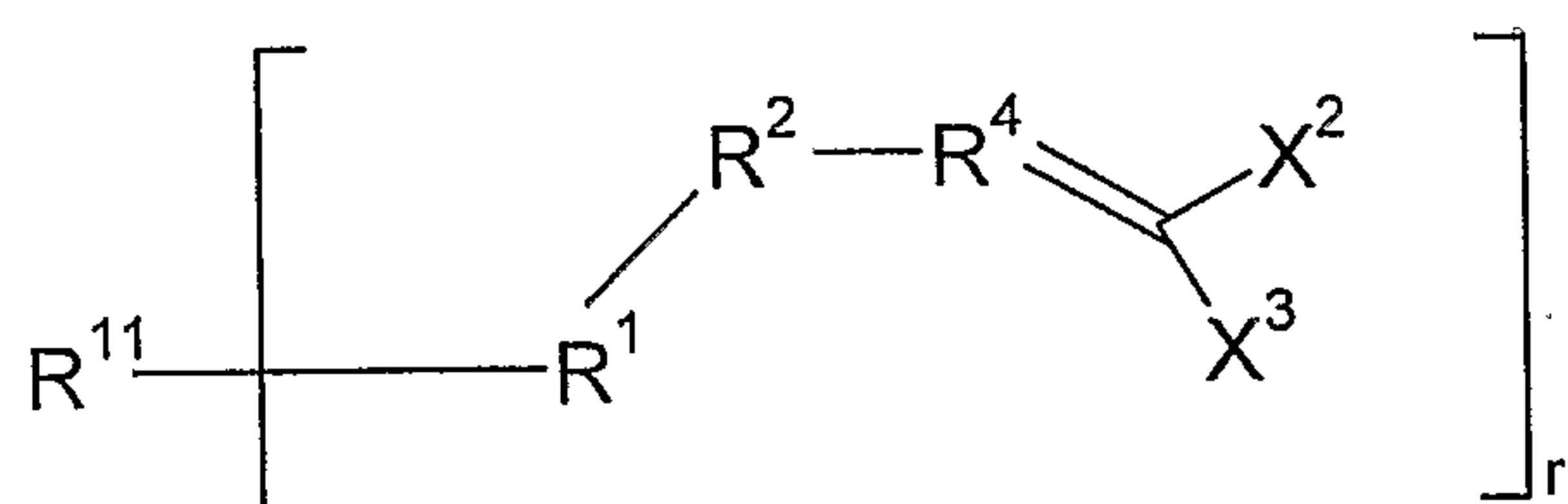
A preferred group of the compounds for use in the method of the invention is a compound of structure (II)

10



(II)

and in particular a compound of formula (IIA)

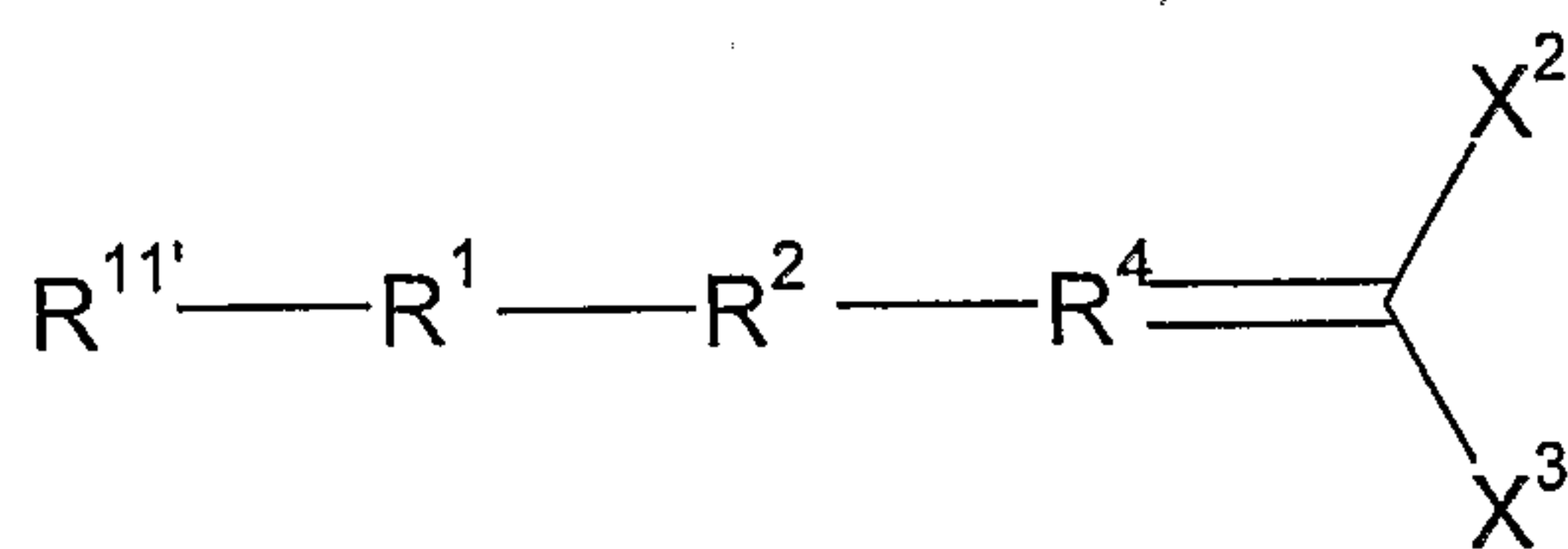


(IIA)

5 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 .

10 Where in the compound of formula (II) and (IIA) 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.

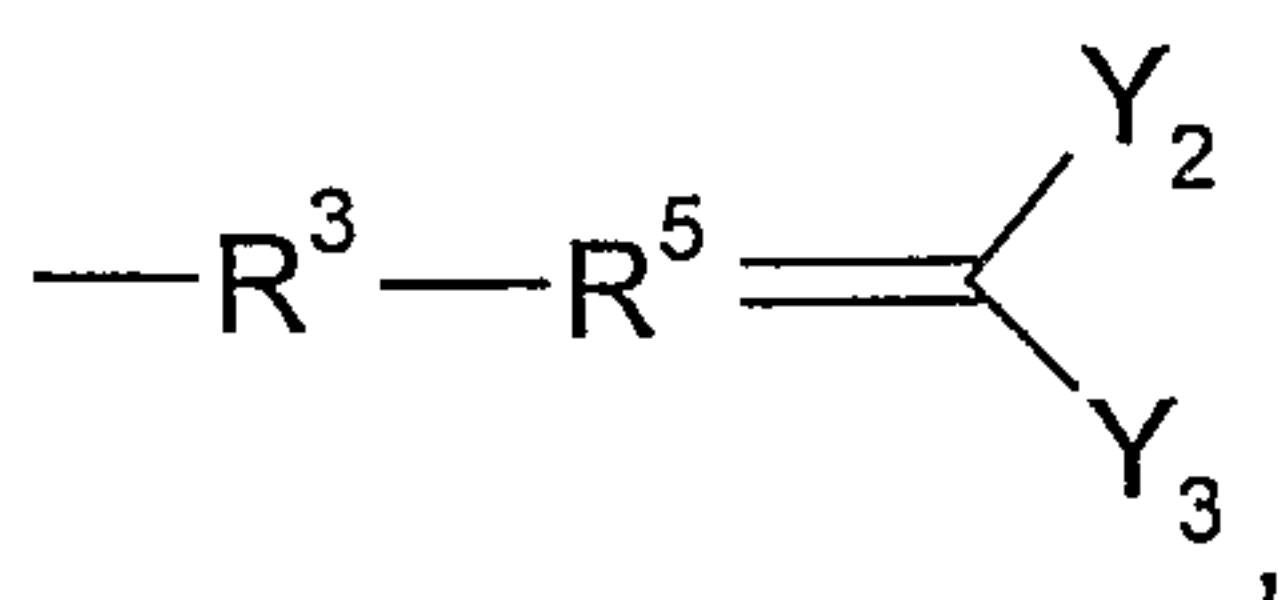
Monomers of this type may be represented as structure (III)



(III)

15

where the group $-\text{R}^3 - \text{R}^5 \equiv \text{Y}^1$, if present, is of the form



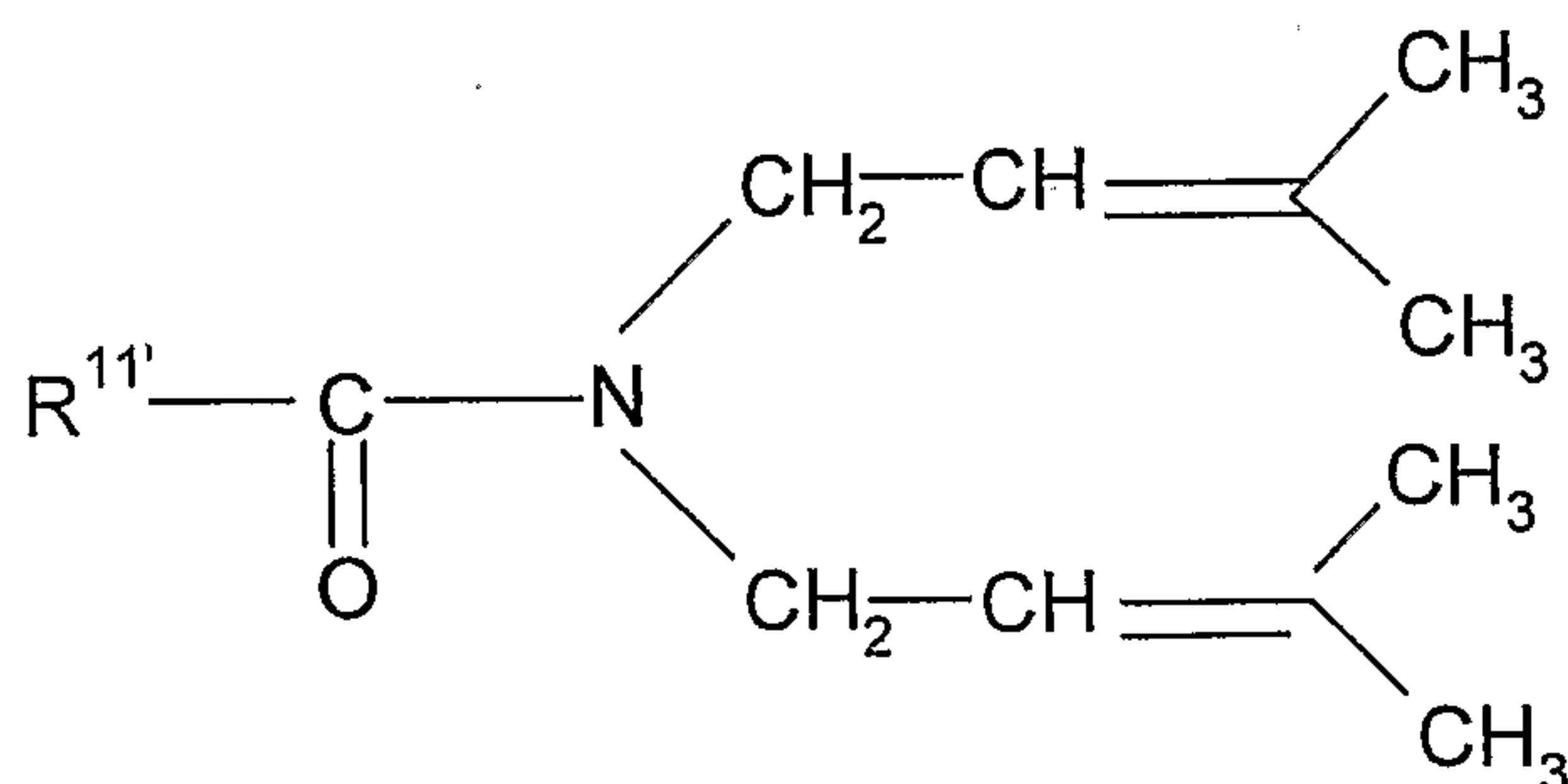
and where X^2 , X^3 , Y^2 , Y^3 , R^1 , R^2 , R^3 , R^4 and R^5 , are as previously defined, and $R^{11'}$ is an optionally substituted hydrocarbyl group, a perhaloalkyl group, a siloxane group or an amide.

- 5 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.

10 In structures of compounds (II), (IIA), (III) and (IV), R^{11} or $R^{11'}$ may comprise a straight or branched chain hydrocarbyl group, optionally substituted or interposed with functional groups.

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.

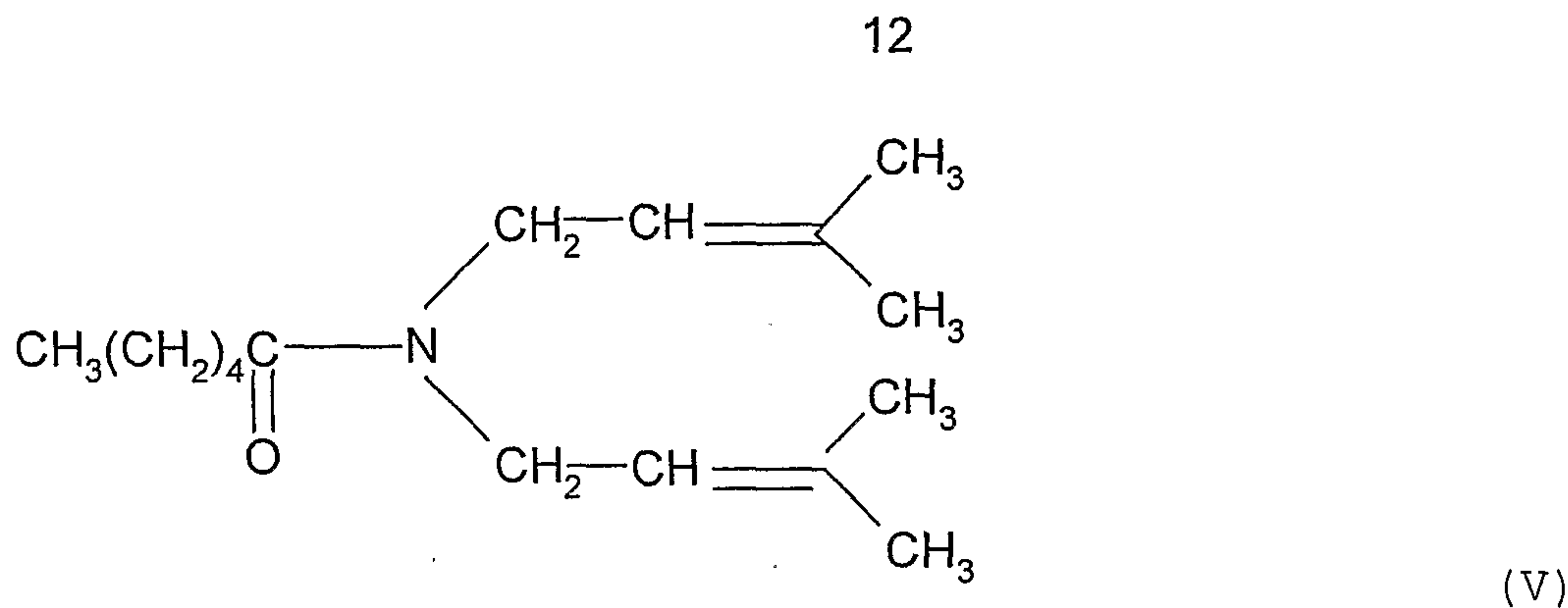
A preferred class of compounds of formula (III) are those of formula (IV)



(IV)

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

The compound of formula (IV) may be of a compound of formula (V)



Alternatively, R^{11} 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.

The invention may also be applied to other sorts of polymers; for example, where in the compounds of formula (II), r is greater than one, polymerisation can result in polymer networks. Particular examples are compounds of formula (II) as defined above, where R^{11} is a bridging group and r is an integer of 2 or more, for example from 2 to 8 and preferably from 2 –4.

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.

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.

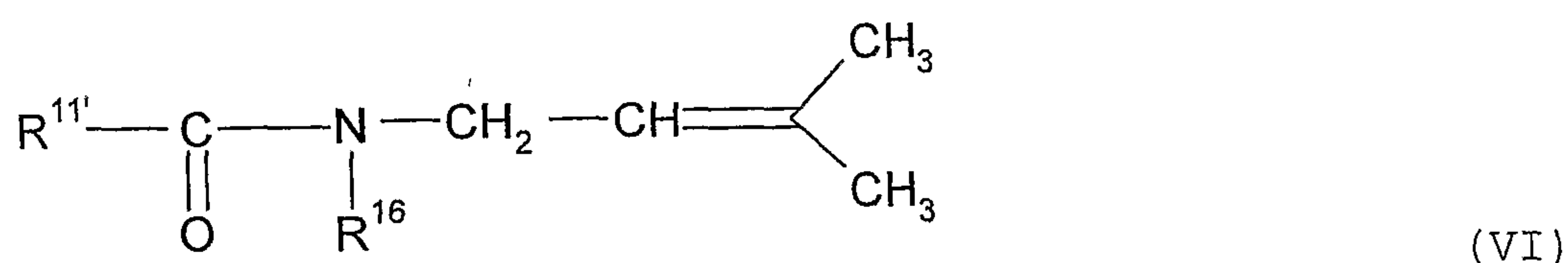
Table 1

Polymer Type	Repeat Unit of Bridging Group
Polyethylene	CH_2
Polystyrene	$\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)$ where the phenyl ring is optionally substituted
Polyisobutylene	$\text{CH}_2\text{CH}(\text{CH}(\text{CH}_3)_2)$
Polyisoprene	$\text{CH}_2\text{CH}(\text{CH}_3)$
Polytetrafluoroethylene	$\text{CH}_2(\text{CF}_2)_x\text{CH}_2$
Polyvinylidene fluoride	$\text{CH}_2(\text{CF}_2\text{CH}_2)_x$
Polyethyleneoxide	$(\text{OCH}_2\text{CH}(\text{CH}_3))_{x0}$
Nylon	$\text{CH}_2(\text{NHCOCH}_2)_x\text{CH}_2$
Peptide	$\text{CH}_2(\text{NHCOCH}_R)_x\text{CH}_2$
Polyurethanes	$-\text{NH}-\text{CO}-\text{O}-$
Polyesters	$-\text{RC}(\text{O})\text{OR}'-$ where R and R' are organic groups such as hydrocarbyl
Polysiloxanes	e.g. $-\text{SiO}_2-$, $-\text{R}_2\text{SiO}-$ or $-\text{R}_2\text{Si}_2\text{O}_3-$ where R is an organic group such as hydrocarbyl
Polyacrylates	$-\text{CH}_2\text{C}(\text{COOH})\text{H}-$
Polyureas	$-\text{NHCONH}-$
Polythioureas	$-\text{NH}-\text{C}(\text{S})-\text{NH}-$

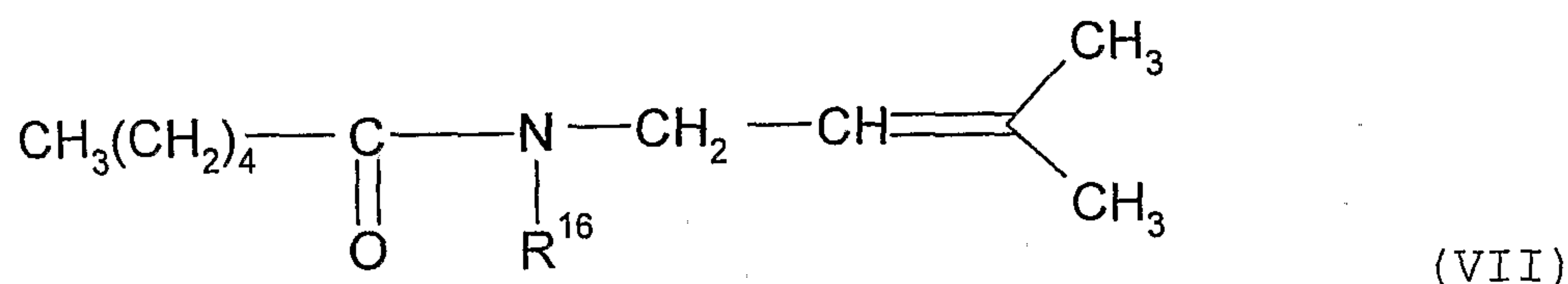
The polymerisation of the starting material may produce a homopolymer.

However, the invention includes the possibility of producing copolymers where another monomeric compound, for example one which is not of formula (I), is mixed with the compound of formula (I) prior to polymerisation. Such monomers are known in the art.

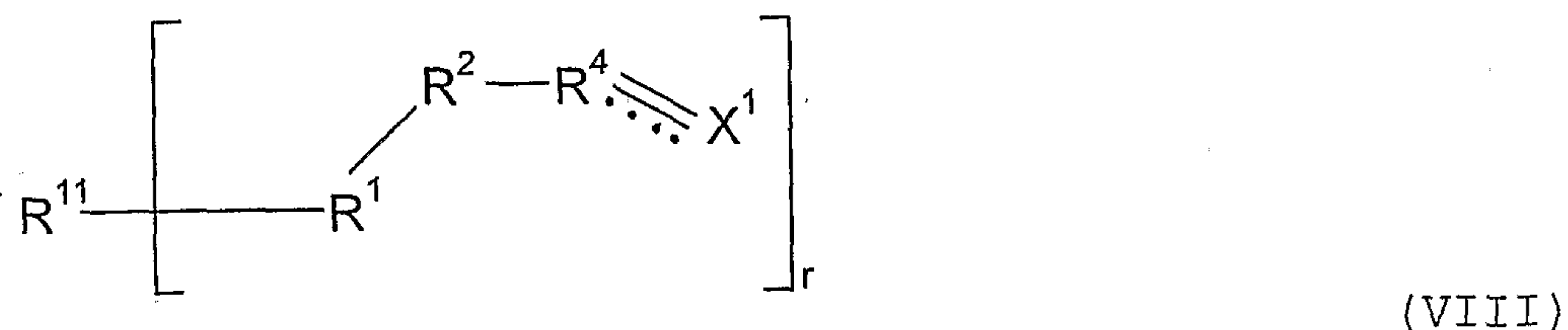
5 In a range of embodiments, the starting material does not include the group $-R^3-R^5\equiv Y^1$. In a preferred example within this range of embodiments, the compound of formula (III) is a compound of formula (VI)



10 where R^{16} is selected from hydrogen, halo, nitro, or hydrocarbyl, optionally substituted or interposed with functional groups, only. The compound of formula (VI) may be a compound of formula (VII)



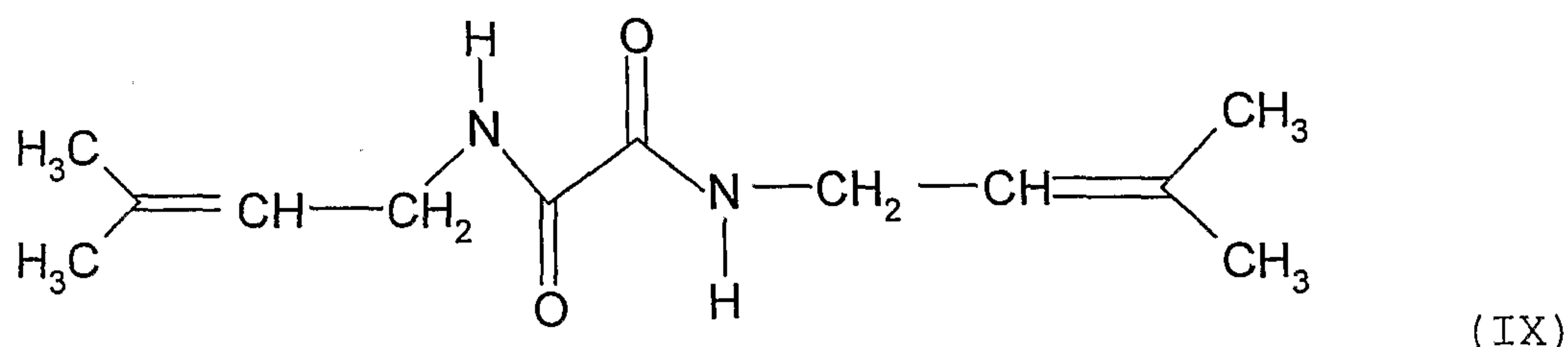
15 In a copolymerisation scheme, a starting material which does not include the group $-R^3-R^5\equiv Y^1$ is reacted with a compound of formula VIII



where R^1 , R^2 , R^4 , R^{11} and X^1 are as defined in relation to sub-formula (I).

Preferably, in formula VIII, r is 2.

The compound of formula (VIII) may be a compound of formula (IX)



Composites may also be produced by polymerising compounds of formula (I) 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.

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.

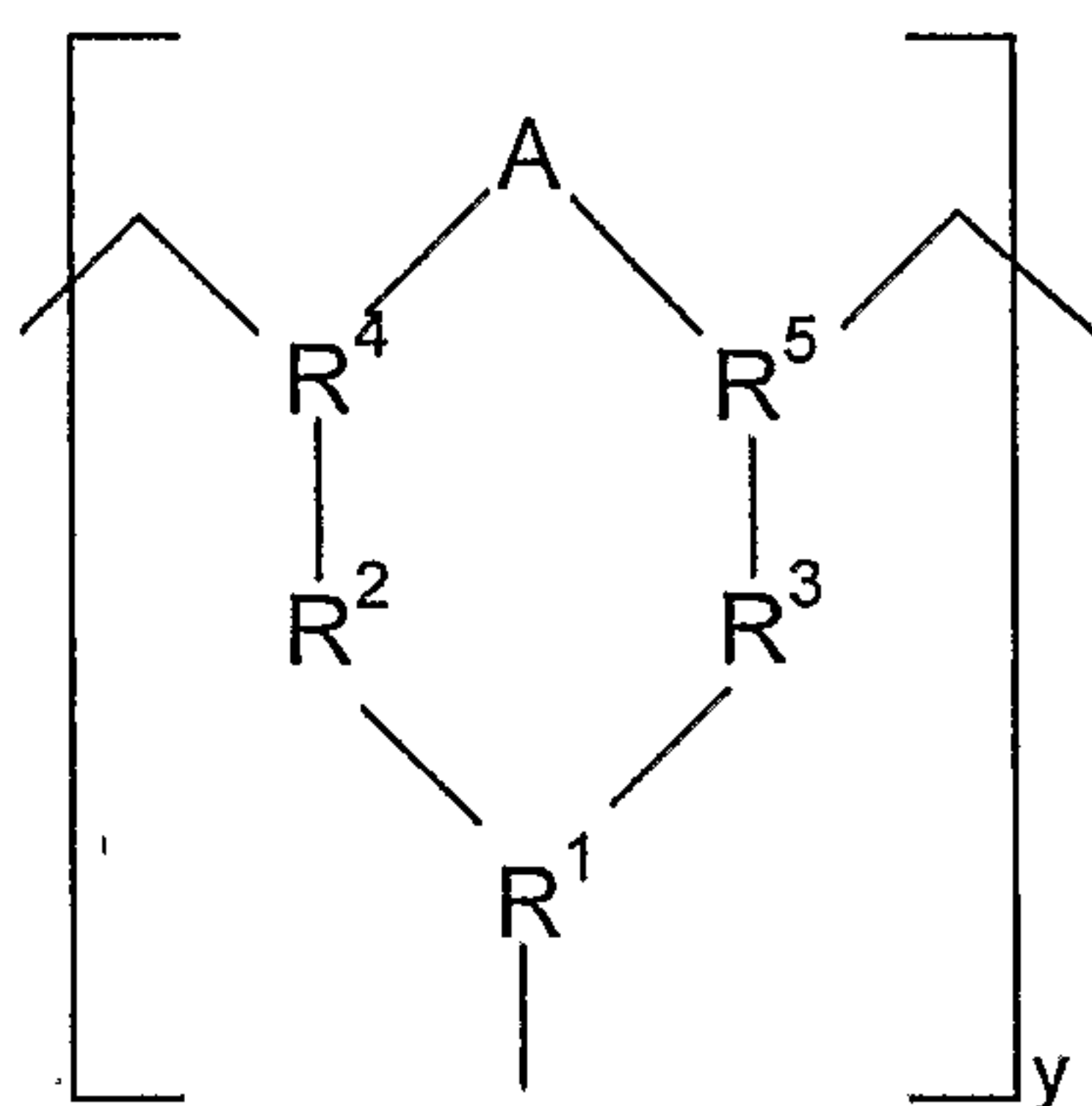
The advantages of the compounds of the invention is that they allow for the possibility that they can be applied in the form of a paint and caused to polymerise in situ. This allows for ease of processing. Further, by providing for the construction of networks as a result of the cross linking, the resultant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

16

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.

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.

5 The polymer may be of sub-formula (X)

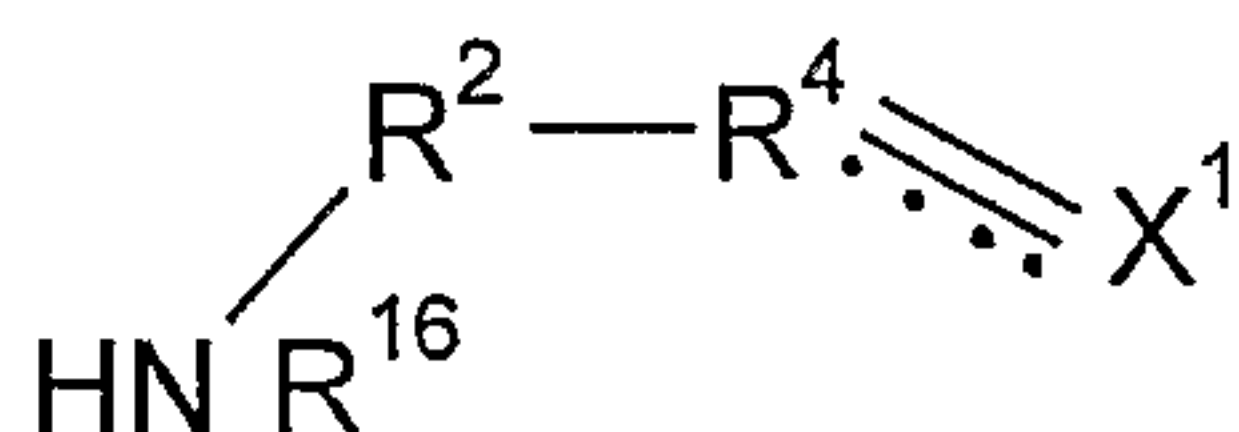


(X)

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

10 According to a third aspect of the invention there is provided a monomeric compound which includes a group of sub-formula (I) 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.

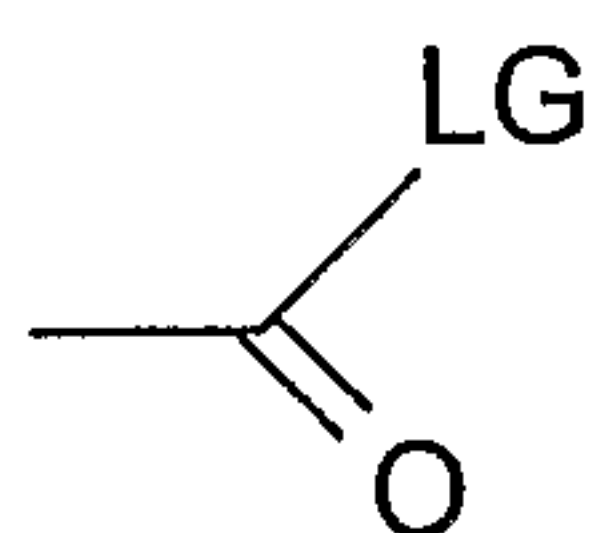
15 According to a fourth aspect of the invention there is provided a method of preparing a monomeric compound in accordance with the third aspect of the invention including the step of reacting a compound having a group of sub-formula (XI)



(XI)

17

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



(XII)

where X^1 , Y^1 , R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are as defined in the first aspect of the invention, and LG is a leaving group.

5 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.

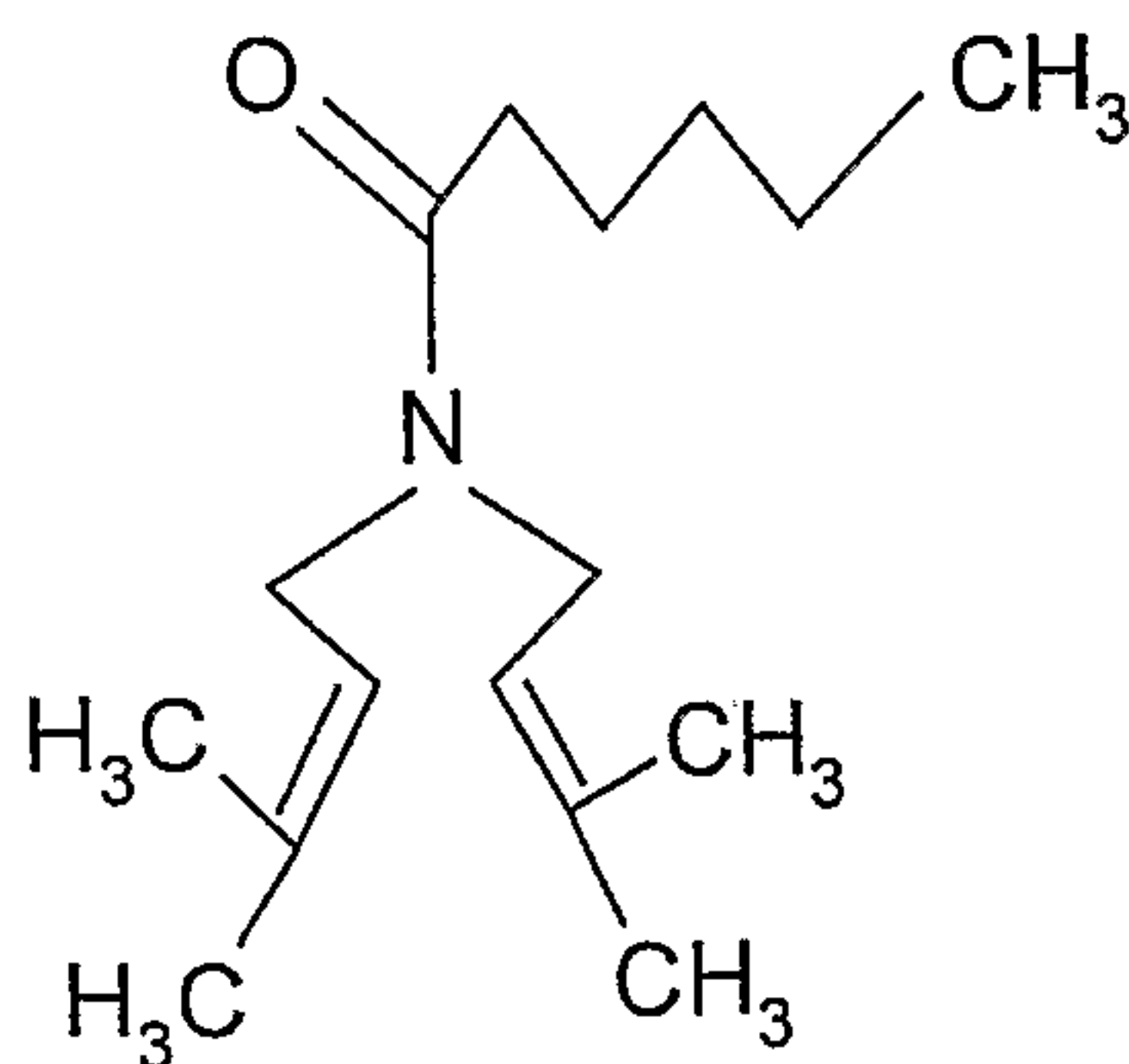
10 Embodiments of monomers, polymers, and methods for preparing same will now be described with reference to the accompanying drawings, in which:-

Figure 1 shows a first reaction scheme; and

Figure 2 shows a second reaction scheme.

Example 1

15 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.

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 CaSO_4 overnight, passed through alumina and fractionally
5 distilled, pyridine was dried over LindeTM type 4A molecular sieves followed by distillation, tetrahydrofuran (THF) was refluxed over sodium-benzophenone mixture before collection.

Column chromatography was carried out using flash grade silica.

10 1.1 Synthesis of 1-bromo-3-methylbut-2-ene(2)

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 (21 g, 22ml, 0.267 moles) was added and the contents of the flask were stirred at room temperature for 30 minutes
15 after which time PBr_3 (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
20 mixture was quenched by the addition of saturated NaCl solution with stirring (1 L).

The organic layer was separated and aqueous layer extracted with t-buytl methyl ether (3 x 300ml). Combined organic layers were washed twice with saturated NaHCO_3 (2x 500ml) followed by water (2x 200ml) then with brine (500ml). The ether layer was dried over anhydrous MgSO_4 and solvent removed under atmospheric pressure. The
25 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 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
10 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
15 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)

Crude tertiary amine (9g, 41mmol) was placed in a 25 ml round bottomed (RB) flask fitted with a condenser. The contents of the flask were heated in a
20 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.

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

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%.

Example 2

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

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.

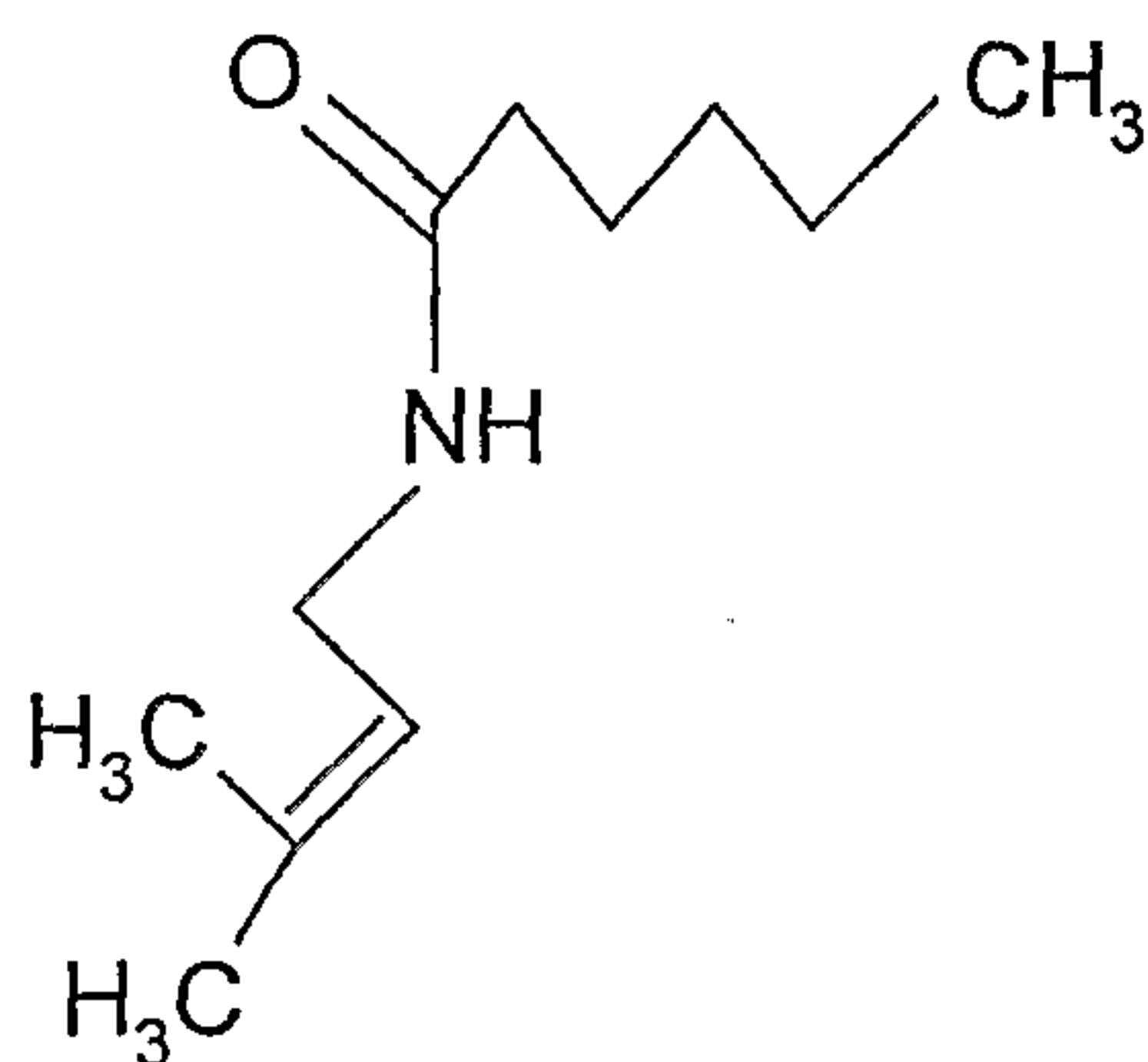
Example 3

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

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

The target molecule 5 (hexanoic acid (bis (3-methylbut-2-enyl) amide) is shown below

5

and the synthetic scheme is shown in Figure 2.

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

3-methyl-buten-3-ol (97%, 500ml) was added to hydrobromic acid (48%, 1L) 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)

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)

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.

Example 5

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

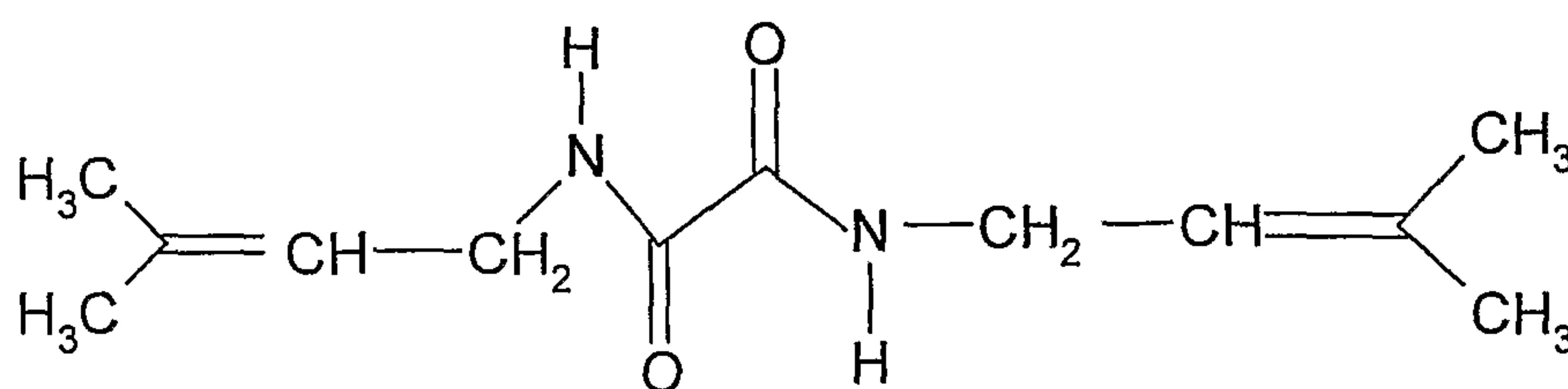
The monomer 5 polymerised under UV radiation using the conditions described in Example 2.

Example 6

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

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

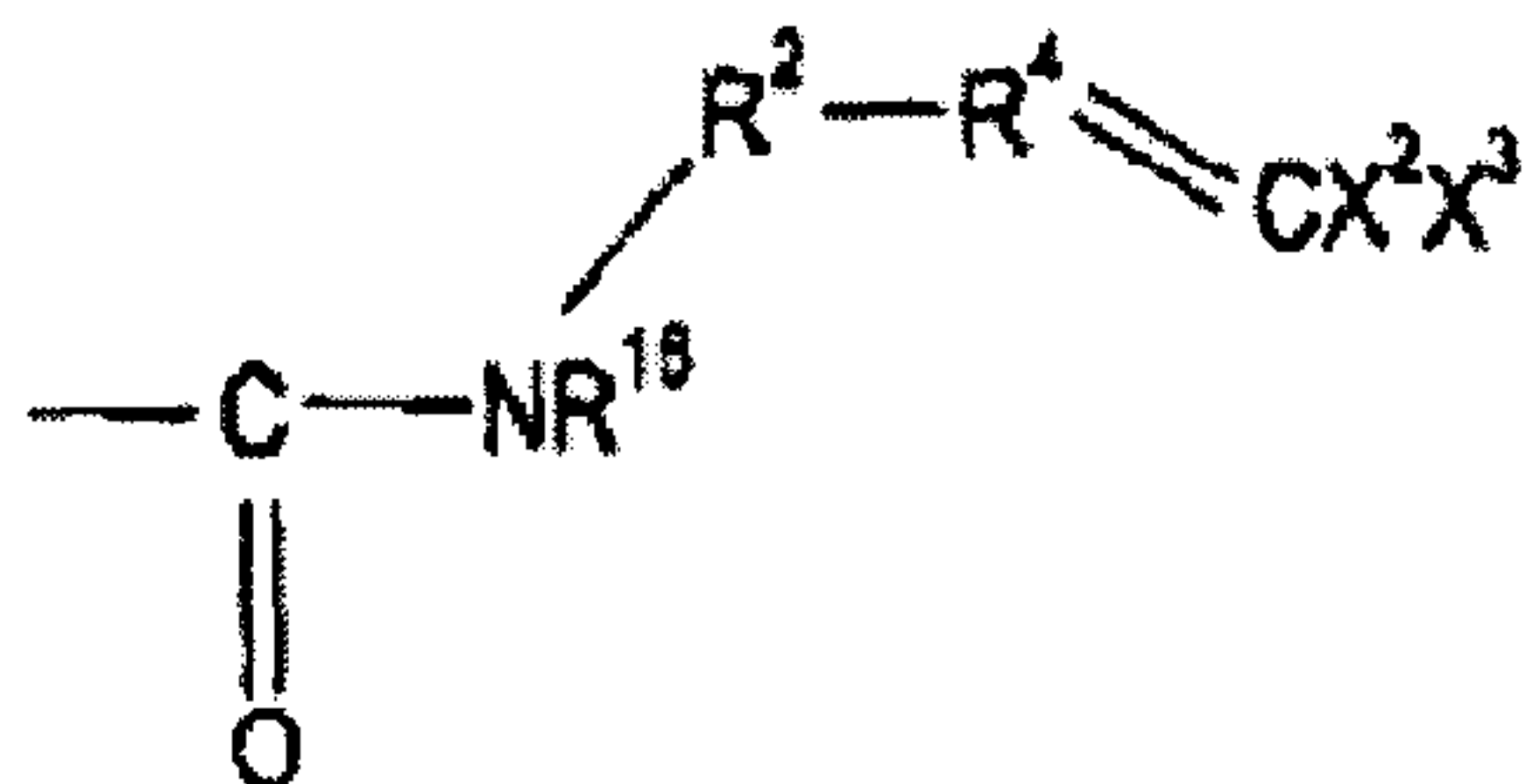
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The cross-linker compound was prepared using the methodology described in Example 4, with the exception that the hexanoyl chloride used in step 4.3 was replaced with oxaloyl chloride (ClO₂CCO₂Cl) in a molar ratio of 2:1 (primary amine 7: oxaloyl chloride). 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.

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)



(XIII)

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

R^2 and R^3 are independently selected from $(\text{CR}^6\text{R}^7)_n$ or a group CR^8R^9 , $\text{CR}^6\text{R}^7\text{CR}^8\text{R}^9$ or $\text{CR}^8\text{R}^9\text{CR}^6\text{R}^7$ 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 CH or CR^{10} where CR^{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.

2. A method according to claim 1 in which X^2 , X^3 , Y^2 and Y^3 are each either methyl or ethyl.

3. A method according to claim 2 in which X^2 , X^3 , Y^2 and Y^3 are each methyl.

4. A method according to any one of claims 1 to 3 in which the group of sub-formula (XIII) includes the group $-\text{R}^3-\text{R}^5=\text{CY}^2\text{Y}^3$, the polymerisation of the starting material is a cyclopolymerisation reaction, and at least one of (a) R^2 and R^3 or (b) R^4 and R^5 includes an electron withdrawing group which is able to activate a cyclopolymerisation reaction.

5. A method according to any one of claims 1 to 4 in which the

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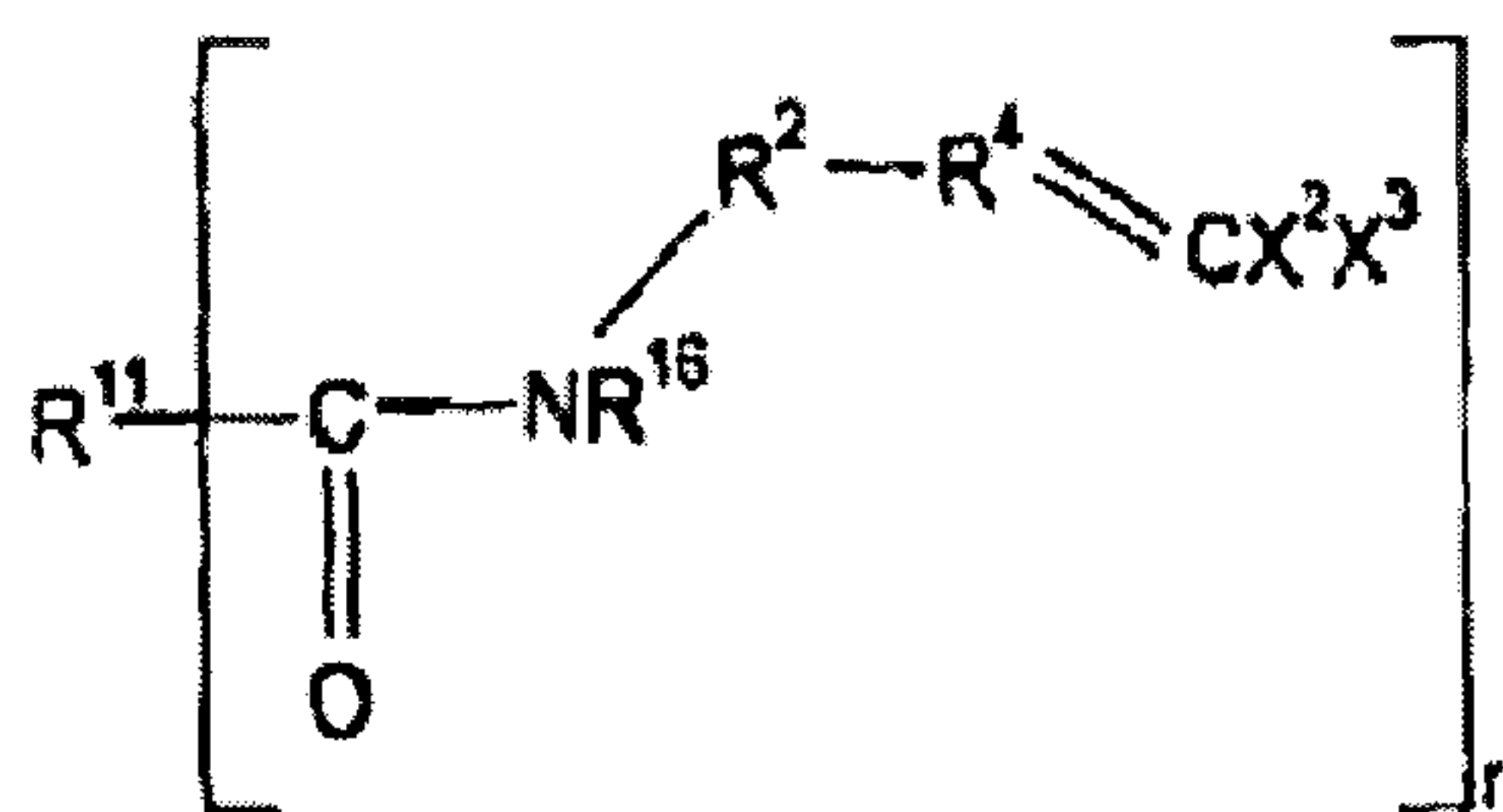
polymerisation of the starting material is effected by the application of radiation, where necessary in the presence of an initiator.

6. A method according to claim 5 wherein the polymerisation is effected by the application of ultraviolet radiation.

5 7. A method according to any one of claims 1 to 4 wherein the polymerisation of the starting material is effected by the application of heat, where necessary in the presence of an initiator.

8. A method according to any one of claims 1 to 4 wherein the polymerisation of the starting material is effected by the presence of a chemical initiator or an electron beam.

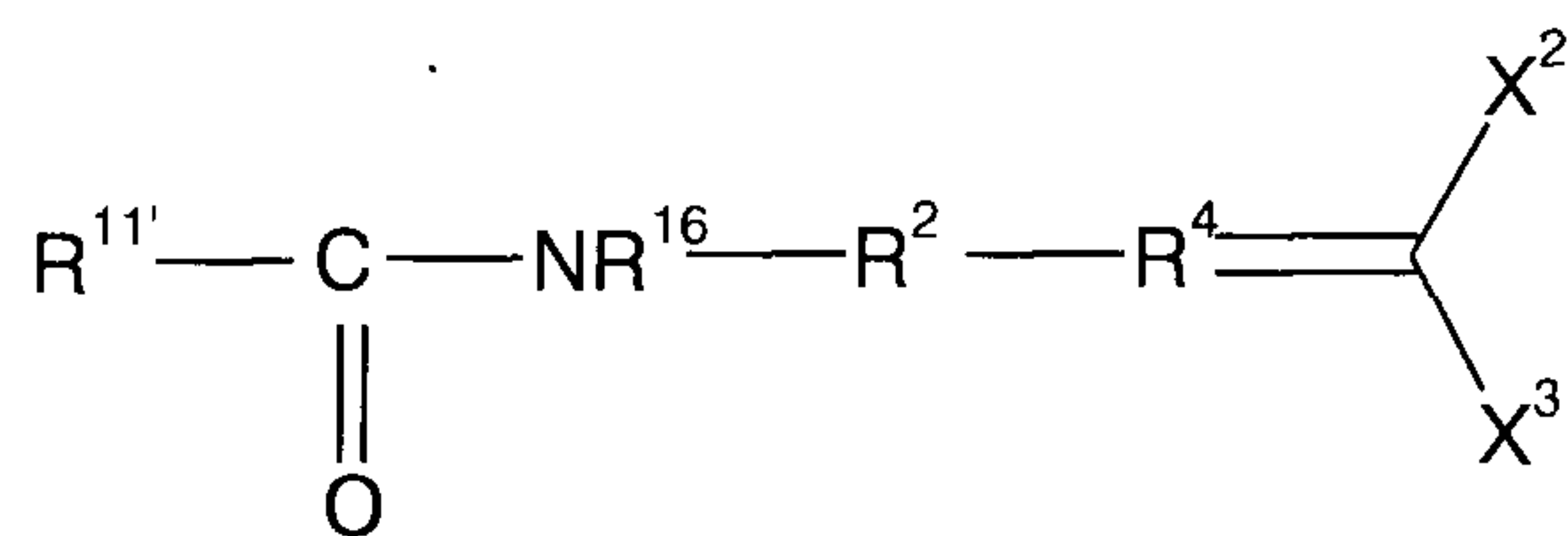
9. A method according to any one of claims 1 to 8 wherein the starting material is a compound of structure (XIV)



(XIV)

15 where R^2 , R^4 , R^{16} , X^2 and X^3 are as defined in claim 1, 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 .

10. A method according to claim 9 wherein the starting material comprises a compound of formula (XV)



(XV)

20 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 $\text{R}^{11'}$ is an

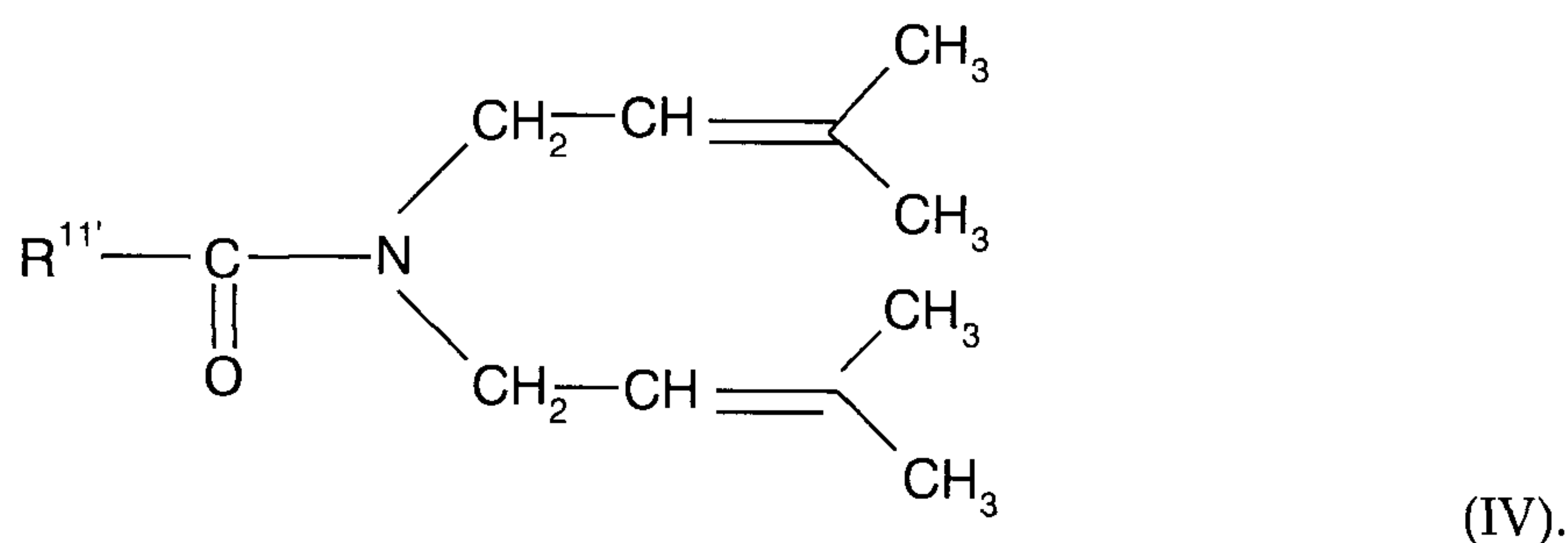
optionally substituted hydrocarbyl group, a perhaloalkyl group, a siloxane group or an amide.

11. A method according to claim 9 or claim 10 in which R^{11} or $R^{11'}$ comprises a straight or branched chain hydrocarbyl group, optionally substituted or interposed with functional groups.

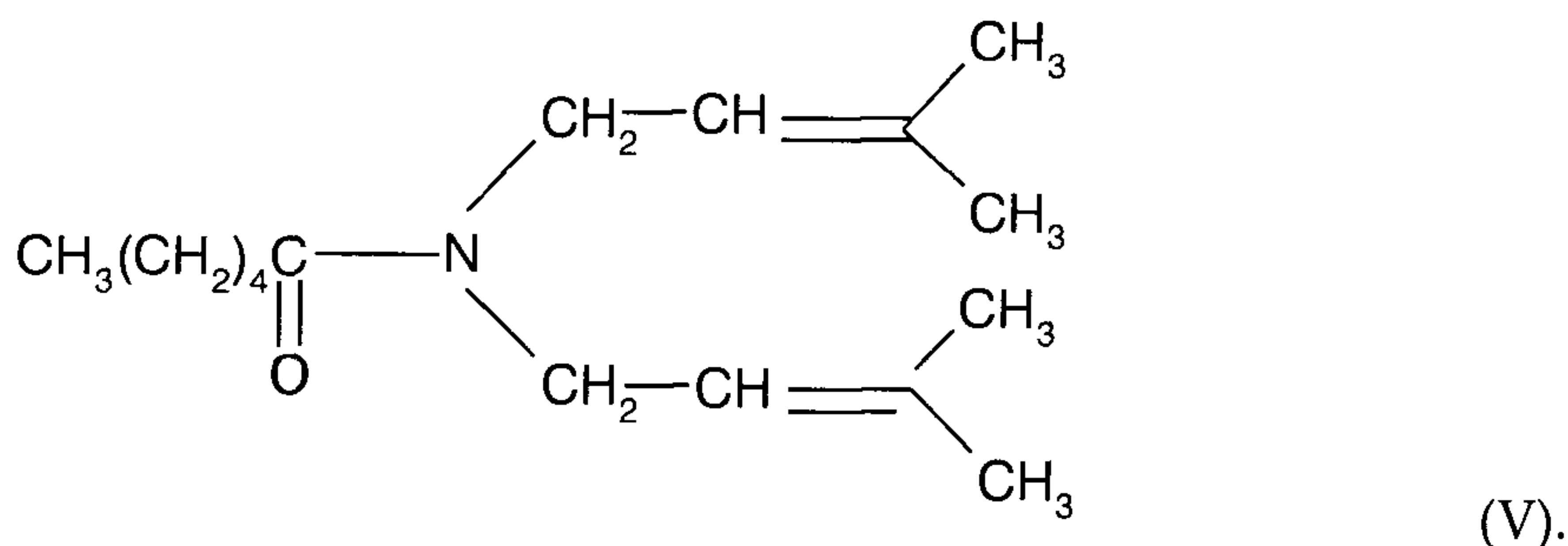
12. A method according to claim 11 in which R^{11} or $R^{11'}$ is an optionally substituted hydrocarbyl group having four or more carbon atoms.

13. A method according to claim 12 in which R^{11} or $R^{11'}$ is a straight or branched chain alkyl group having four or more carbon atoms.

14. A method according to any one of claims 10 to 13 wherein the compound of formula (XV) is a compound of formula (IV)



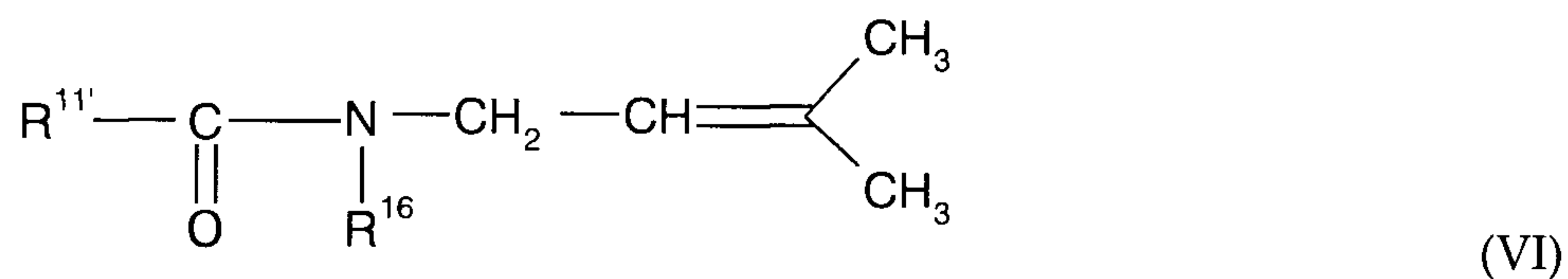
15. A method according to claim 14 in which the compound of formula (IV) is a compound of formula (V)



16. A method according to any one of claims 1 to 13 in which the starting material does not include the group $-R^3-R^5=CY^2Y^3$.

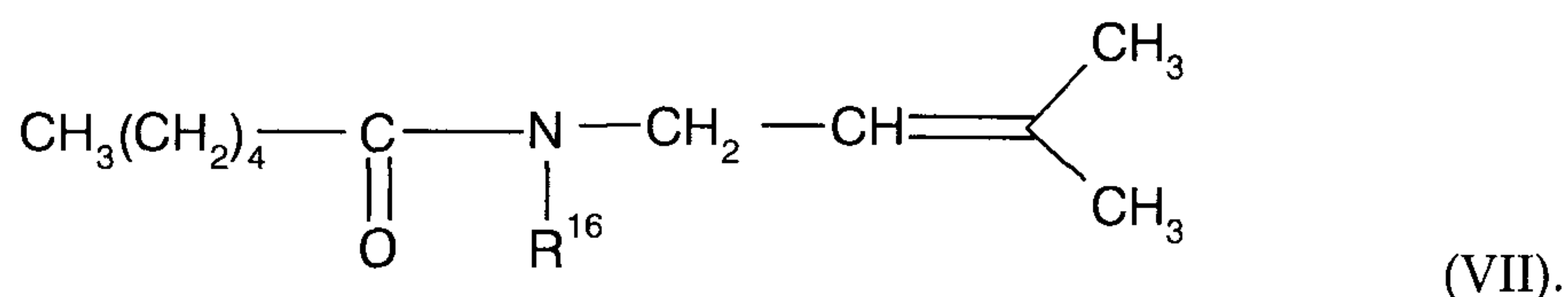
17. A method according to claim 16 when dependent on any one of claims 10

to 13 wherein the compound of formula (XV) is a compound of formula (VI)



where R^{16} is selected from hydrogen, halo, nitro or hydrocarbyl, optionally substituted or interposed with functional groups, only.

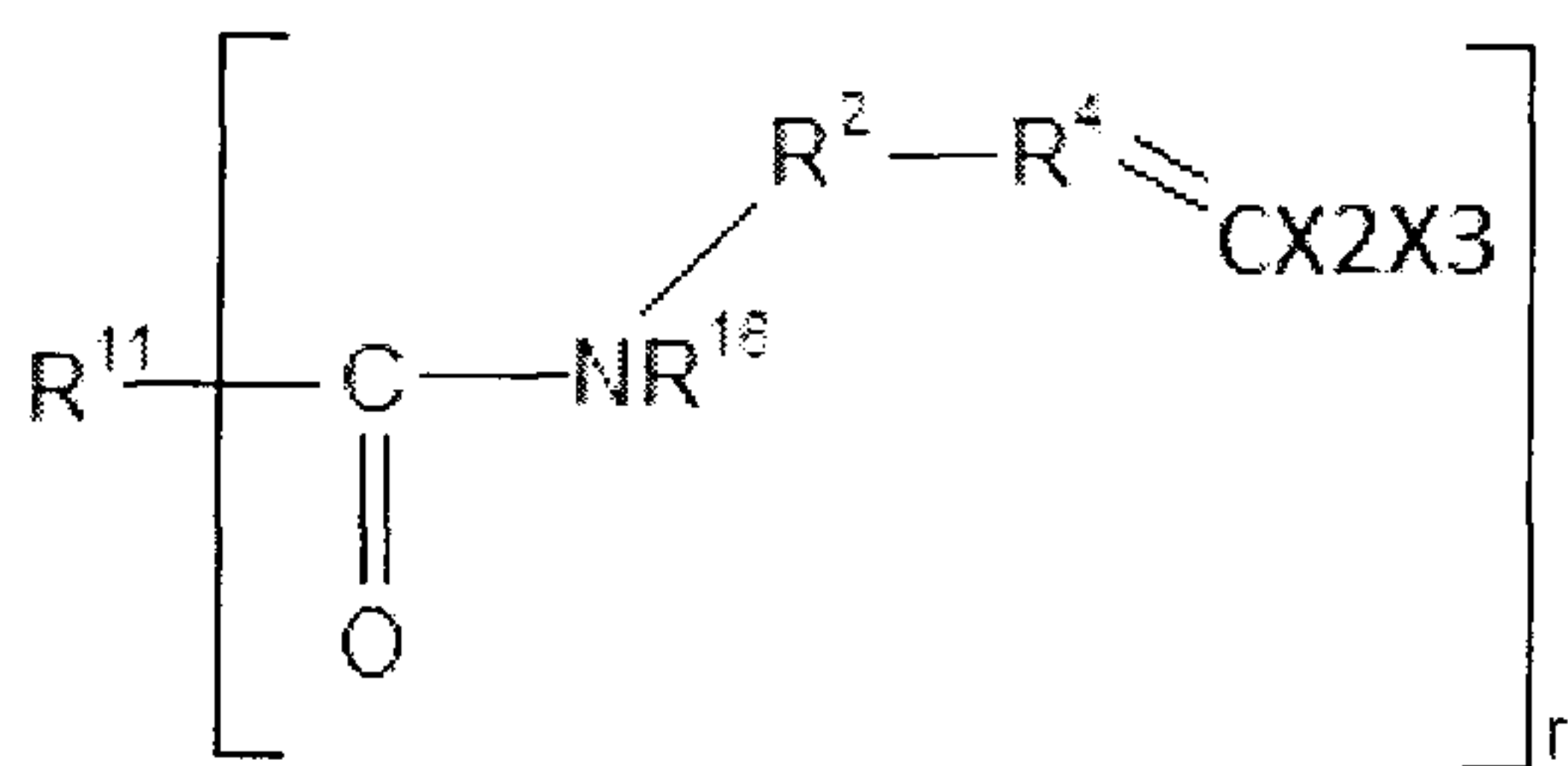
18. A method according to claim 17 in which the compound of formula (VI) is a compound of formula (VII)



19. A method according to any one of claims 1 to 18 wherein the polymerisation of the starting material produces a homopolymer.

20. A method according to any one of claims 1 to 18 wherein the step of polymerising the starting material produces a copolymer, the starting material being mixed with different monomeric units.

21. A method according to claim 20 when dependent on any one of claims 16 to 18 in which the starting material is reacted with a compound of formula XVI



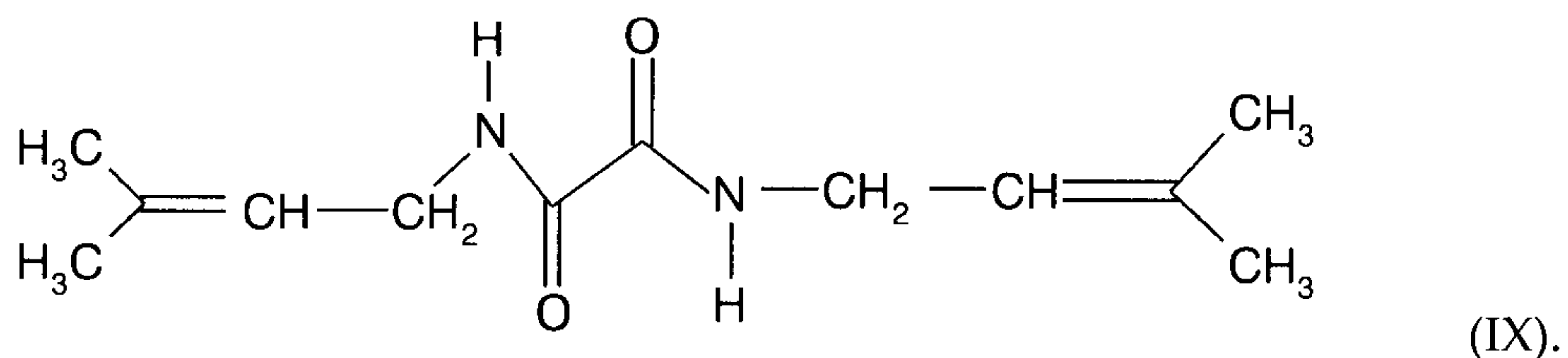
(XVI)

where R^2 , R^4 , R^{16} , X^2 and X^3 are as defined in Claim 1, R^{11} is as defined in Claim 9,

and r is an integer of 1 or more.

22. A method according to claim 21 in which r is 2.

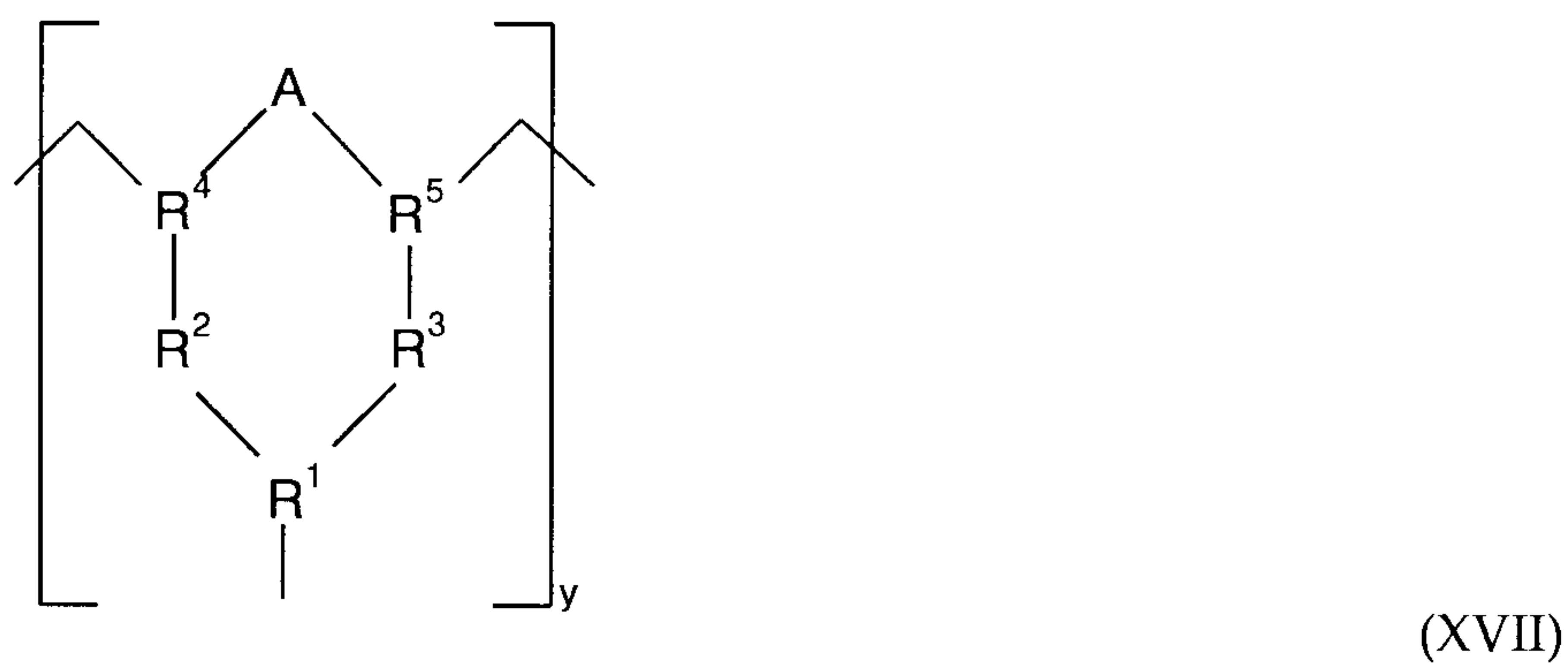
23. A method according to claim 21 in which the compound of formula VIII is a compound of formula (IX)



24. A method according to any one of claims 1 to 23 wherein the starting material is applied to a substrate prior to polymerisation and the polymerisation results in the production of a coating on the substrate.

10 25. A polymer obtained by a method according to any one of claims 1 to 24.

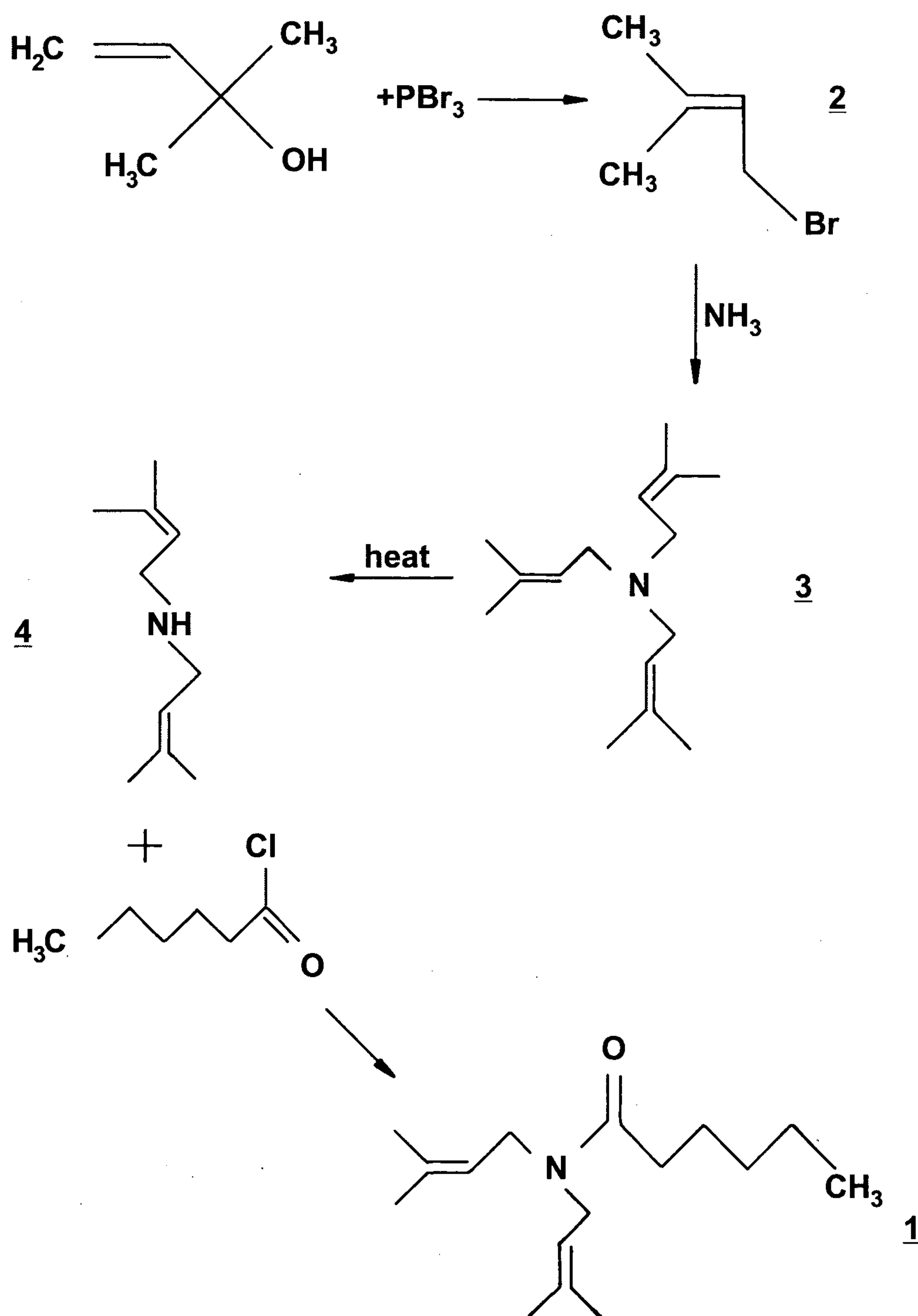
26. A polymer according to claim 25 of sub-formula (XVII)



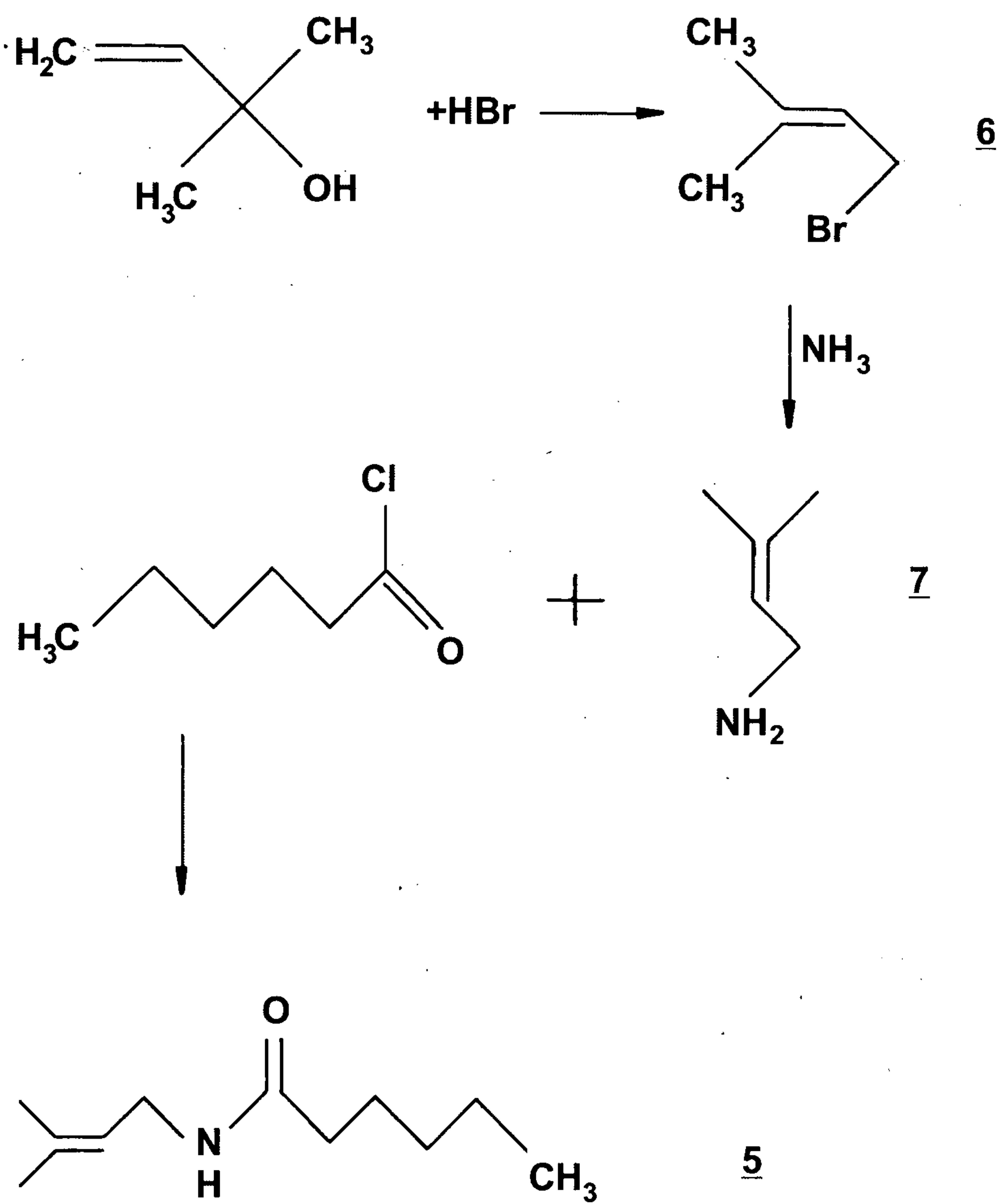
where A is a bond or CY^2Y^3 , R^2 , R^3 , R^4 , R^5 , and CY^2Y^3 are as defined in Claim 1, and y is an integer in excess of 1.

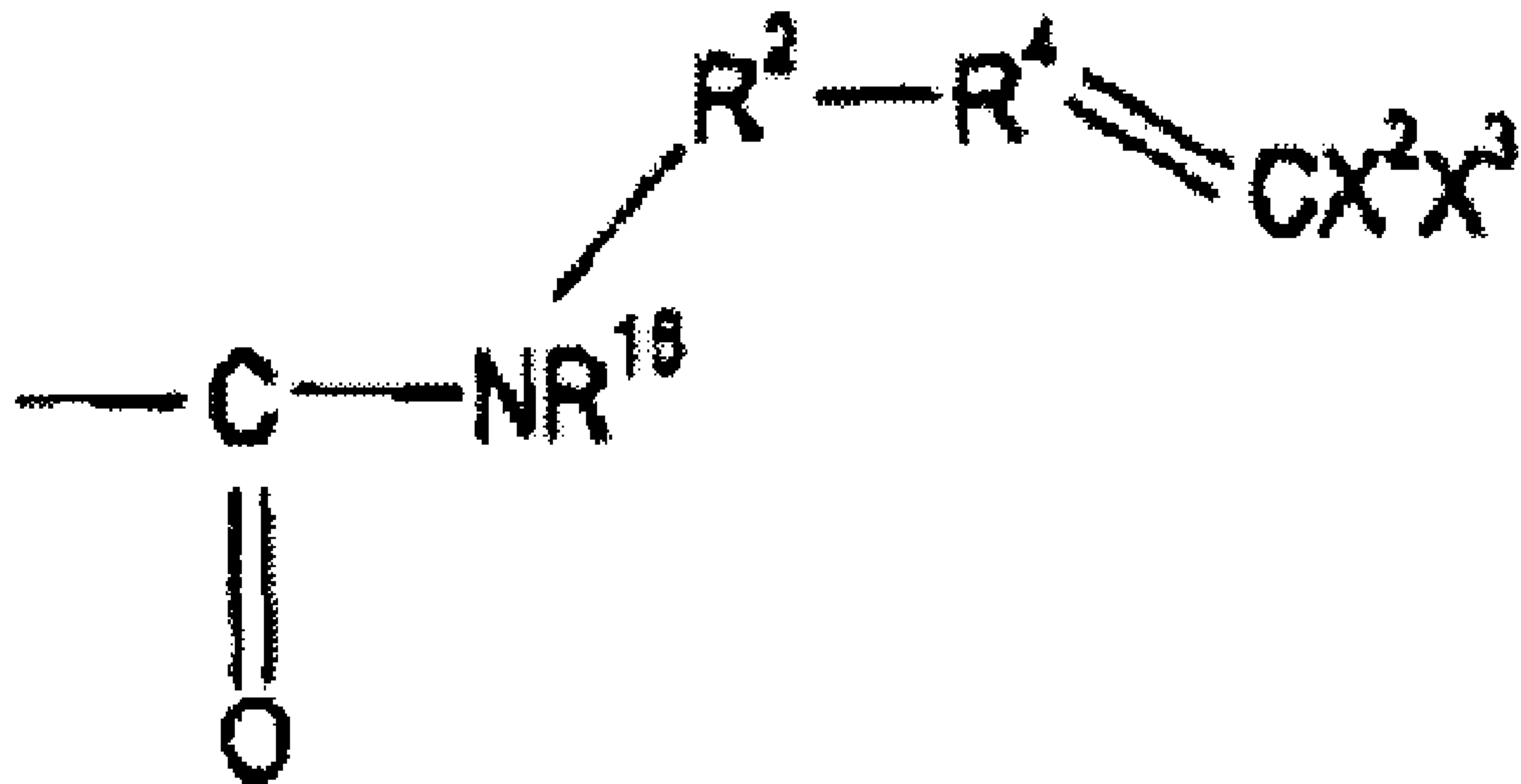
27. A monomeric compound which includes a group of sub-formula (XIII) as defined in claim 1.

1/2

**Fig. 1**

2/2

*Fig. 2*



(XIII)