

Preparation of hydrogen bridge-forming monomers and supramolecular polymers

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(57) Abstract Supramolecular polymer containing monomeric units that form H-bridges with one another, the H-bridge-forming monomeric units in pairs forming at least 4 H-bridges with one another. Preferably, the H-bridge-forming monomeric units are self-complementary and constitute an essentially flat structure. Polymers according to the invention may be composed in several ways. The polymers may consist substantially of H-bridge-forming monomeric units with a low molecular weight, as a result of which an essentially linear polymer may be formed; also conceivable on the other hand are (essentially linear) polymers in which the H-bridge-forming monomeric units are linked to 2 ends of the polymers so that polymeric chains are linked to one another via the H-bridges. In addition, a number of H-bridge-forming monomeric units can be grafted onto polymers, so that a form of cross-linking via H-bridges may be obtained.		

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SUPRAMOLECULAR POLYMER

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The invention relates to a supramolecular polymer containing monomeric units that form H-bridges with one another.

Such polymers are described in Lehn J.-M. Angew. Chem. 1988, 100.91, which describes polymers based on monomeric units that form 3 H-bridges with one another.

A drawback of the polymers described in the aforementioned publication is that even these 3-fold H-bridges do not associate sufficiently for many possible applications of supramolecular polymers. It has been found that no association constants higher than 10^5 M^{-1} can be realized for 3-fold H-bridges with neutral molecules. These supramolecular polymers have thus shown no properties characteristic of polymers with only covalent bonds between the monomers. In addition, the synthesis of the building blocks that associate the most strongly is particularly difficult and cannot be carried out on a large scale.

25 The invention now provides polymers containing H-bridge-forming monomeric units in which the bond via the H-bridges is much stronger than with the known supramolecular polymers.

This is achieved according to the invention by using H-bridge-forming monomers which, in pairs, form at least 4 H-bridges with one another.

The term "supramolecular polymer" is understood to mean an organic compound that obtains its polymeric properties, for example with respect to mechanical strength, etc., essentially through a combination of covalent bonds and secondary specific interactions, the latter preferably having a high bond

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strength and contributing substantially to the polymeric behaviour.

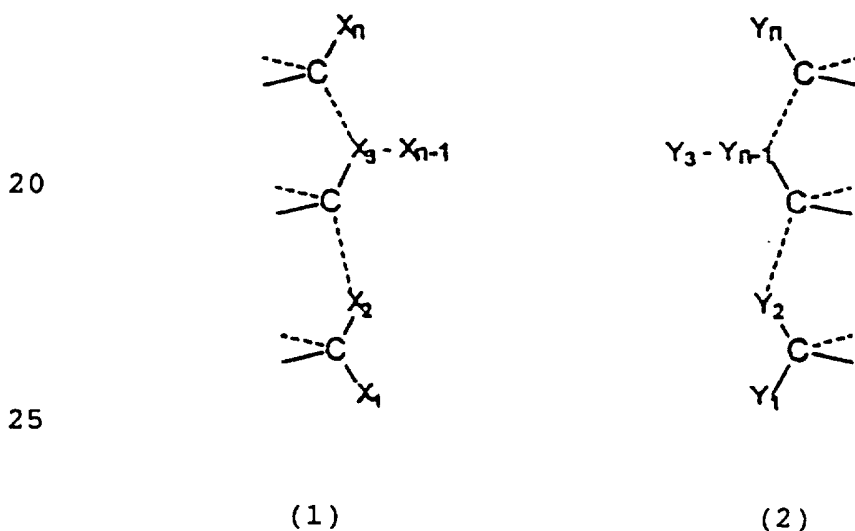
There has for many years been an interest in supramolecular polymers in which the monomers are at least in part bound to one another via H-bridges.

Advantages of such polymers are that, in principle, materials with polymeric properties can be obtained in which the bond via the H-bridges can be used in a reversible manner, and that the polymer can be composed from simple low-molecular-weight units. As the H-bridges are much weaker at higher temperatures, implying a more rapid exchange between monomers than at low temperatures, an important advantage is obtained in processing: at higher temperatures only monomeric units (that can be easily handled) are essentially present which, when the temperature is lowered, form a rigid, dimensionally stable polymer. The "polymerisation step" takes place under mild conditions in comparison with the polymerisation of polymers that are only covalently bound, and is greatly simplified because no catalysts or other additives have to be added.

In a supramolecular polymer, H-bridge-forming monomeric units are, with the exception of the polymeric ends, bound via at least 2 bonds ("on at least 2 sides"). An H-bridge-forming monomeric unit is in the context of this invention understood to be a unit that is on at least one side linked via at least 4 H-bridges to another H-bridge-forming monomeric unit in the supramolecular polymer, and is moreover on at least one side bound in the supramolecular polymer via a different, for example covalent, bond. In the case of a linear supramolecular polymer consisting exclusively of H-bridge-forming monomeric units the H-bridge-forming monomeric units are for example bound on 2 sides to the adjacent H-bridge-forming monomeric unit, with there being a covalent bond on one side and on the other side a bond via at least 4 H-bridges.

The H-bridge-forming monomeric units that can be used in the process according to the invention may be self-complementary, which means that at least 2 identical monomeric units form at least 4 H-bridges with one another; it is however also possible for the supramolecular polymer to contain 2 (or more) different types of H-bridge-forming monomeric units, with 2 different monomeric units always forming at least 4 H-bridges with one another. A combination is of course also possible. Preferably, the H-bridges are oriented parallel to one another. Particularly suitable H-bridge-forming monomeric units are those units that contain a structural element having the general form (1) or (2)

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in which the C- X_i and C- Y_i linkages each represent a single or double bond, n is 4 or more and $X_1 \dots X_n$ represent donors or acceptors that form H-bridges with the H-bridge-forming monomeric unit containing a corresponding structural element (2) linked to them, with X_1 representing a donor and Y_1 an acceptor and vice versa.

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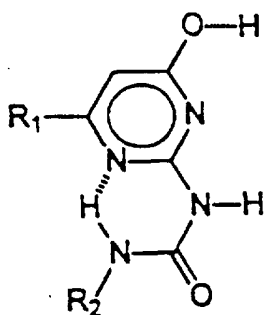
The H-bridge-forming monomeric units preferably have an essentially flat, rigid structure;

in particular, the monomeric unit preferably contains one or more flat 6-rings and/or one or more H-bridges. In a linear supramolecular polymer the bonds preferably associate via the H-bridges only in the direction of
5 the supramolecular polymer chain.

The invention is in particular aimed at H-bridge-forming monomeric units having 4 donors or acceptors, so that they can in pairs form 4 H-bridges with one another. Preferably the H-bridge-forming
10 monomeric units have 2 successive donors, followed by 2 acceptors, for example monomeric units according to formula 1 with $n = 4$, in which X_1 and X_2 both represent a donor and an acceptor, respectively, and X_3 and X_4 both an acceptor and a donor, respectively.

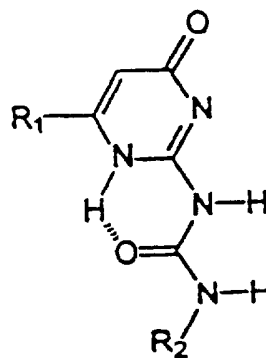
15 A particularly suitable H-bridge-forming monomeric unit that can be used in the polymers according to the invention is the compound (3.a) or the tautomeric form (3.b) thereof:

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3.a



3.b

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The H-bridge-forming monomeric units according to formulas 3.a and 3.b, respectively, may be bound in the supramolecular polymer in various ways. These H-bridge-forming monomeric units may for example
35 be bound in the supramolecular polymer via a linking unit R_2 , with R_1 representing a random side chain, or vice versa, while it is also possible for the

supramolecular polymer to contain linkages via both R_1 and R_2 .

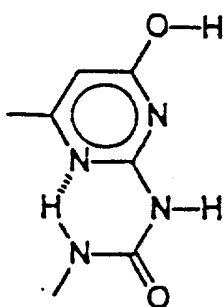
As side chains, R_1 and R_2 may in principle represent any group that is inert in the formation of the supramolecular polymer, for example an alkyl, alkoxy or aryl group, whether or not substituted, or groups containing esters or ethers; the side chain may however also be a polymeric chain. The number of C atoms in these groups is in no way critical and lies for example between 1 and 40 C atoms, in particular between 1 and 20 C atoms. Preferably the side chain is an alkyl group.

As linking units, R_1 and R_2 may also represent all kinds of shorter or longer chains, for example saturated or unsaturated alkyl chains, siloxane chains, ester chains, ether chains and any chain of atoms used in traditional polymer chemistry, whether or not substituted.

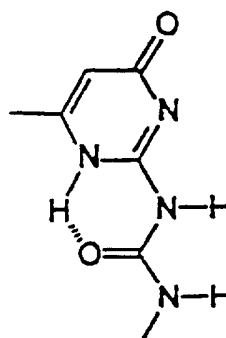
These self-complementary compounds can be easily prepared on a large scale and can be easily modified.

The invention also relates to compounds containing structural elements having the general formula 4.a or 4.b.

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4.a.

4.b.

where --- stands for an H-bridge.

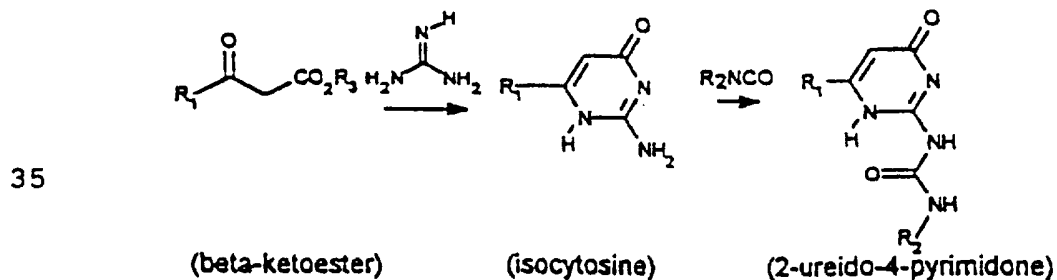
Polymers according to the invention may be composed in several ways. The polymers may consist substantially of H-bridge-forming monomeric units with a low molecular weight, optionally mixtures of such H-bridge-forming monomeric units, as a result of which an essentially linear polymer may be formed; also conceivable on the other hand are (essentially linear) polymers in which the H-bridge-forming monomeric units are linked to 2 ends of the polymers so that polymeric chains are linked to one another via the H-bridges. In addition, a number of H-bridge-forming monomeric units can be grafted onto polymers, as a result of which a form of cross-linking via H-bridges may be obtained. Mixed forms are of course also possible. Both low- and high-molecular, linear or branched polymers can be used as the polymers, for example polymers known from traditional polymer chemistry, or mixtures of such polymers.

The invention will now be elucidated with reference to the examples; without however being limited thereby.

Examples

25 Synthesis units

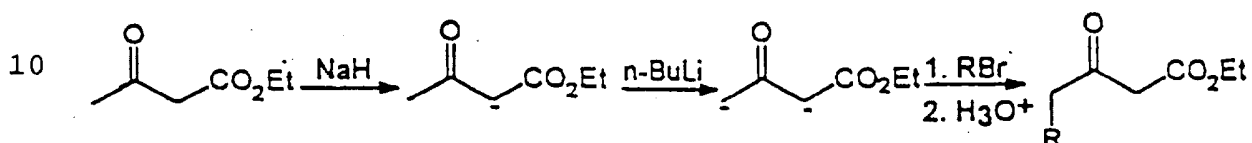
The 2-butylureido-4-pyrimidone unit can be quickly prepared by causing precursor isocytosine to react with isocyanate in refluxing pyridine. Isocytosines can in turn be easily prepared from β -keto esters through condensation with guanidine.



β -keto esters can be synthesised in several manners. Two of the most frequently used manners are (a) alkylation of the dianion of (m)ethyl acetoacetate with an alkyl halide, and (b) reaction of an acid chloride

5 with the anion of ethyl acetoacetate, followed by deacylation of an aceto fragment.

The reaction scheme for a is as follows:

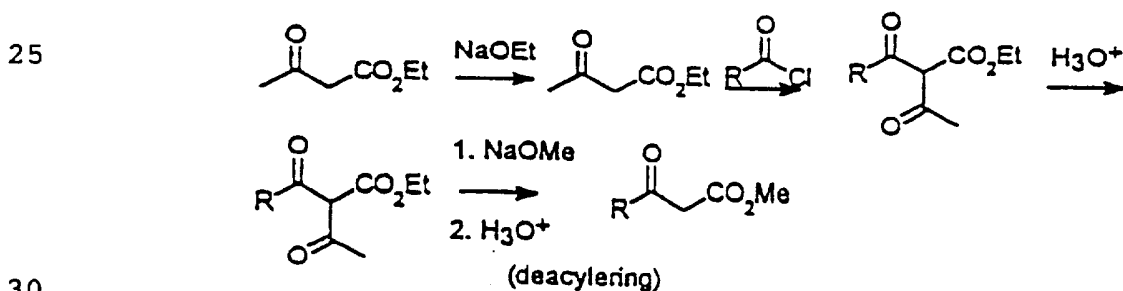


The anion of ethyl acetoacetate is first prepared in THF with the aid of sodium hydride, after which the dianion is prepared with the aid of butyl lithium. This dianion is caused to react with an alkyl halide, in which process it reacts at the 4-position, the most nucleophilic position. Working-up takes place through neutralisation with acid of the monoanion still

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20 present.

The reaction scheme for b is as follows:



First the anion of the ethyl acetoacetate is prepared in ether using sodium ethoxide in ethanol. This nucleophilic anion attacks the electrophilic carbon of the acid chloride, the chloride being eliminated. At

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least 2 equivalents of base are required per acid chloride, because the neutral product formed initially

immediately donates a proton to the anion of ethyl acetoacetate or ethoxide. An excess of ethyl acetoacetate is also important, because the ethoxide is more nucleophilic than the anion of ethyl acetoacetate. By using an excess of ethyl acetoacetate relative to ethoxide, the undesired formation of an ethyl ester through reaction of the ethoxide with the acid chloride is thus prevented. After the reaction the anion is neutralised with acid. Next, deacylation takes place with the aid of sodium ethoxide in methanol, the ester being largely converted from an ethyl ester into a methyl ester. Sodium ethoxide in methanol is used for the deacylation instead of sodium ethoxide in ethanol, because the deacylation does not proceed well with the latter. It is however not important whether methyl or ethyl ester is formed, in view of the fact that in the formation of the isocytosine (m)ethanol is eliminated anyway.

20 Experimental methods

General experimental section

Dry tetrahydrofuran (THF) was obtained through distillation in the presence of sodium and benzophenone. Dry toluene was obtained through distillation and freezing. Pyridine, ethanol and dimethylformamide (DMF) (p.a.) were dried using 4 A molecular sieves.

Kieselgel 60 F₂₅₄ aluminium plates were used for thin-layer chromatography (TLC). UV-active compounds were identified with the aid of 254 nm UV. Merck Kieselgel 60 with a particle size of 63-200 μm and Merck Kieselgel 60H with a particle size of 40-63 μm were used for column chromatography.

NMR spectra were recorded with the aid of a Varian Gemini (300 MHz) or a Bruker AC400 (400 MHz). Chemical shifts (δ) for both proton and carbon are indicated in ppm relative to tetramethylsilane (TMS).

Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

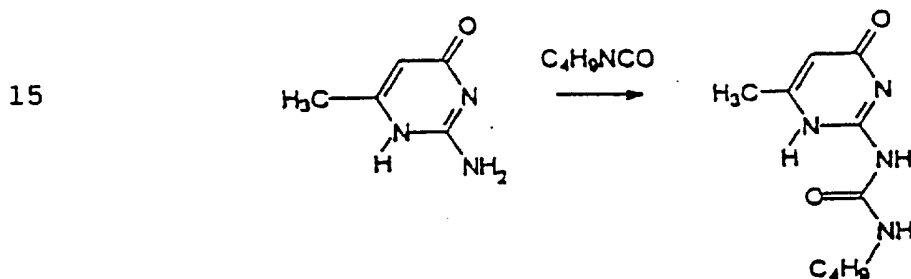
Infrared (IR) spectra were recorded with the aid of a Perkin-Elmer 1600 FT-IR spectrometer.

5 A Perkin-Elmer DSC 7 was used in DSC analysis.

Melting points were determined with the aid of a Jenaval THMS 6000 polarisation microscope.

10 Example I

2-butylureido-6-methyl-4-pyrimidone



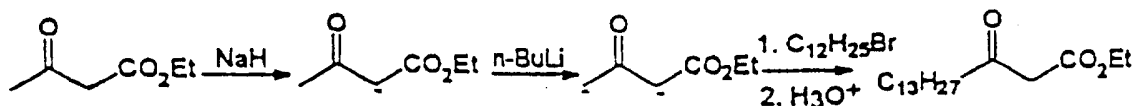
6-methyl-isocytosine (commercially available) was weighed into a flask (1.24 grams, 0.018 mol). The flask was fitted with a reflux condenser with a nitrogen inlet tube and was brought under a nitrogen atmosphere. 25 50 ml of dry pyridine was added, followed by butyl isocyanate (2 ml, 0.018 mol). The suspension was heated to reflux temperature, during which a clear solution was slowly obtained (after approx. 1 hour). After 2 30 hours' boiling while refluxing, the solvent was evaporated, after cooling. The white residue was crystallised from 1/1 v/v ethanol/chloroform. Yield 1.63 grams, 66%.

¹H-NMR (CDCl₃): δ (ppm): 13.15 (s, 1H), 11.85 (s, 1H), 10.16 (s, 1H), 5.81 (s, 1H), 3.24 (q, 2H), 3.22 (s, 35 3H), 1.58 (m, 2H), 1.37 (m, 2H), 0.92 (t, 3H). ¹³C-NMR (CDCl₃): δ (ppm): 173.0, 156.5, 154.7, 148.1, 106.6,

39.7, 31.5, 20.1, 18.9, 13.7, IR (KBr) (keto form): ν (cm^{-1}): 3215, 2954, 2868, 1705, 1666, 1584.

Example II

5 Ethyl 3-oxo-hexadecanoate



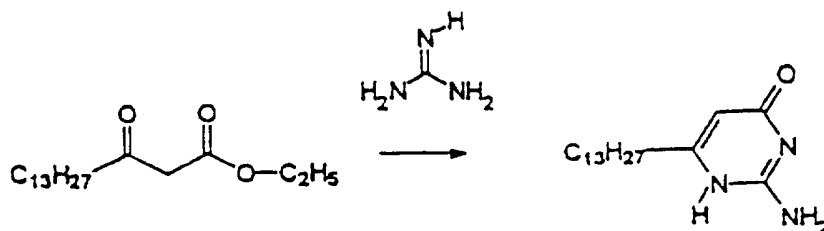
10 Sodium hydride (60%, 4.42 g, 0.11 mol) was weighed into a dry 3-neck flask (1000 cc). The flask was brought under a nitrogen atmosphere and placed in an ice-salt bath, after which dry THF (250 ml) was added at 0°C. Ethyl acetoacetate (13.02 g, 0.102 mol) was added drop
 15 by drop via a dry syringe, at a temperature of between 0 and 5°C. A strongly exothermic reaction took place with gas formation. After 30 minutes' stirring at 0°C, n-butyl lithium (1.6 M, 66 ml, 0.104 mol) was added drop by drop, after which the stirring was continued
 20 for 15 min. at 0°C. Dodecyl bromide (127.4 g, 0.110 mol) in dry THF (20 ml) was added via a dry syringe at 0°C. The solution was stirred for 45 min, during which the temperature rose to room temperature and a suspension formed. To this suspension were added
 25 concentrated hydrochloric acid (20 ml) in water (600 ml), followed by ether (1000 ml). After extraction, the water layer was once again extracted with ether. The combined ether layers were washed with water 5 times. The ether layer was dried over sodium sulphate,
 30 filtered and evaporated. A total of 136.11 grams of crude product was obtained in four such syntheses. NMR showed that the product is a mixture of ethyl 3-oxo-hexadecanoate (61%) and dodecyl bromide (39%), so the corrected ethyl 3-oxo-hexadecanoate yield is 0.29 mol,
 35 72%. The crude product was used as such for the following synthesis. $^1\text{H-NMR}$ (CDCl_3): δ (ppm): 4.16 (t, 2H), 3.38 (s, 2H), 2.52 (t, 2H), 1.82 (m, 2H), 1.58 (m,

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2H), 1.25 (m, 21H) 0.85 (t, 3H).

6-Tridecylisocytosine

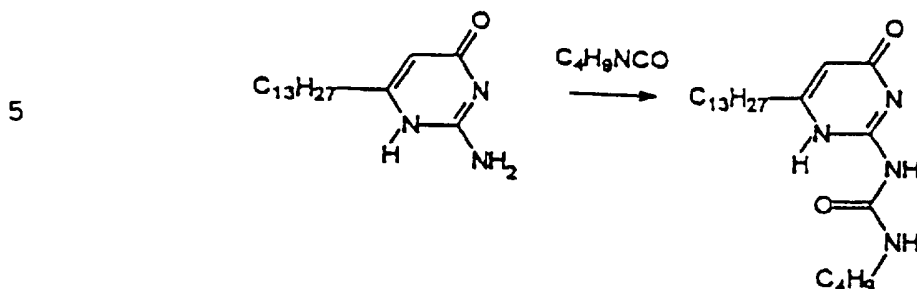
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10 Guanidine carbonate (30.63 g, 0.17 mol) was weighed
into a dry 2-neck flask (500 ml). The flask was brought
under a nitrogen atmosphere, after which dry ethanol
(220 ml) and the crude ethyl 3-oxo-hexadecanoate
(136.11 g, 0.29 mol) were added. After refluxing
15 overnight, ethanol (100 ml) was slowly evaporated and
the refluxing was continued for another 2 hours. After
cooling, hexane (300 ml) was added, followed by water,
which caused 6-tridecylisocytosine to precipitate,
which could be removed through filtration. This was
20 successively washed with hexane, acetone and water.

The crude product was recrystallised from
ethanol with a Norit treatment. The product was
obtained as a microcrystalline powder, after thorough
drying, 39.68 g (0.142 mol, 48%). $^1\text{H-NMR}$ (DMSO d_6): δ
25 (ppm): 10.57 (s, 1H), 7-6 (br, 2H), 5.36 (s, 1H), 2.24
(t, 2H), 1.55 (t, 2H), 1.26 (m, 20H), 0.86 (t, 3H). $^{13}\text{C-}$
NMR (DMSO d_6): δ (ppm), (388 K): 168.1, 162.7, 155.0,
99.2, 36.1, 30.4, 28.1 (overlapping peaks), 26.6
(overlapping peaks), 21.1, 12.6 IR (KBr): ν (cm^{-1}):
30 3365, 3146, 2920, 2850, 2713, 1662, 1639, 1553, 1468,
1400. Element analysis: N 14.65% (calc. 14.32%), C
70.91% (calc. 69.58%), H 11.27% (calc. 10.65%). Melting
point: 181°C.

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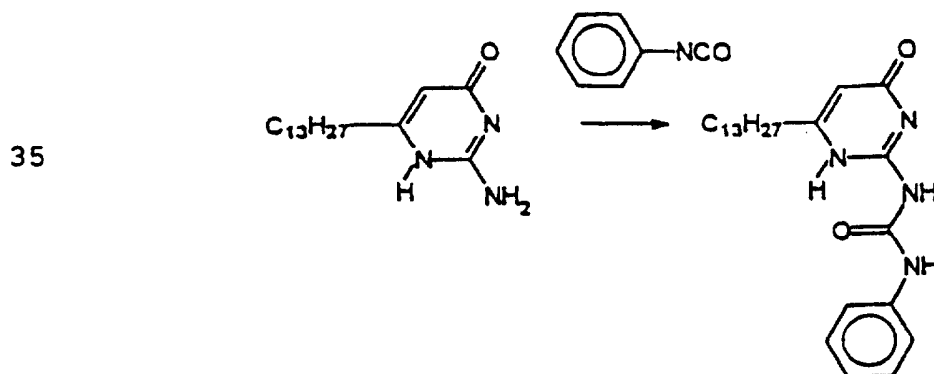
2-butylureido-6-tridecyl-4-pyrimidone

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6-tridecylisocytosine (10.22 g, 0.036 mol) was weighed into a dry 2-neck flask (500 ml). The flask was brought under a nitrogen atmosphere, after which dry pyridine (200 ml) and butylisocyanate (6.8 ml, 0.06 mol) were added. After 4 hours' refluxing, the pyridine and the residual butylisocyanate were evaporated.

Recrystallisation from acetone followed by drying resulted in pure 2-butylureido-6-tridecyl-4-pyrimidone as a microcrystalline powder (11.58 g, 0.0295 mol, 82%). ¹H-NMR (CDCl₃): δ (ppm): 13.18 (s, 1H), 11.88 (s, 1H), 10.17 (s, 1H), 5.82 (s, 1H), 3.24 (q, 2H), 2.45 (t, 2H), 1.62 (m, 4H), 1.31 (m, 22H), 0.90 (m, 6H). ¹³C-NMR (CDCl₃): δ (ppm): 174, 157, 155, 152, 106, 41, 33, 32, 30 (overlapping peaks), 24, 21, 15, 14. IR (KBr) (enol form): ν (cm⁻¹): 3200, 3132, 2920, 2849, 2480, 1666, 1610, 1557, 1453. Element analysis: N 14.35% (calc. 14.27%), C 66.54% (67.31%), H 10.41% (10.27%). Melting point 118°C.

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Example III2-phenylureido-6-tridecyl-4-pyrimidone

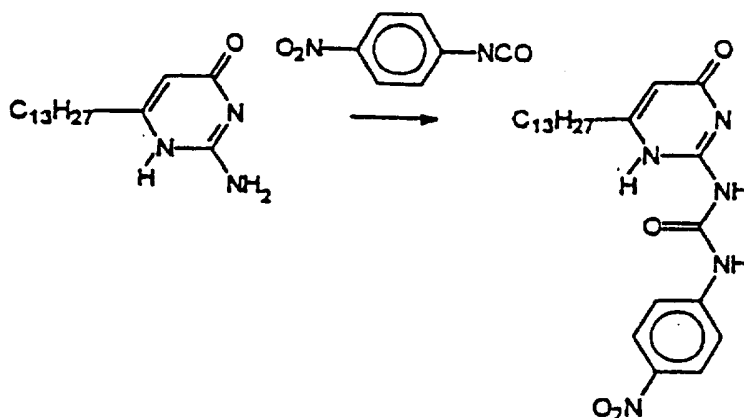
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6-tridecylisocytosine (0.28 g, 0.001 mol) was weighed into a dry 2-neck flask (25 ml). The flask was brought under a nitrogen atmosphere, after which dry pyridine (5 ml) and phenylisocyanate (0.21 ml, 0.0018 mol) were added. After 4 hours' refluxing the mixture was cooled to room temperature and diluted with acetone. The precipitated white powder was filtered. Recrystallisation from acetic acid resulted in pure 2-phenylureido-6-tridecyl-4-pyrimidone as a microcrystalline powder (0.14 g, 0.00034 mol, 34%). $^1\text{H-NMR}$ (CDCl_3): δ (ppm): 12.99 (s, 1H), 12.21 (s, 1H), 12.19 (s, 1H), 7.70 (d, 2H), 7.34 (t, 2H), 7.09 (t, 1H), 5.83 (s, 1H), 2.31 (t, 2H), 1.53 (m, 2H), 1.26 (m, 20H), 0.90 (t, 3H). $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm): 173.0, 154.6, 152.8, 138.2, 128.9, 123.9, 120.6, 106.0, 32.5, 31.9, 29.6, 29.6, 29.4, 29.4 (overlapping peaks), 29.2, 28.8, 26.6, 22.7, 14.1. IR (KBr) (keto form): ν (cm^{-1}): 3133, 3022, 2918, 2849, 1701, 1654, 1560, 1500.

20 Example IV

2-(p-nitrophenyl)ureido-6-tridecyl-4-pyrimidone

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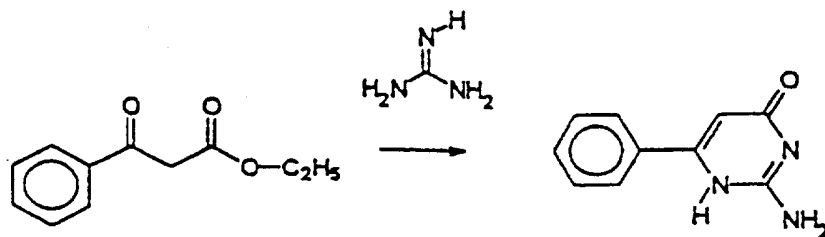


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6-tridecylisocytosine (0.44 g, 0.00015 mol) was weighed into a dry 2-neck flask (100 ml). The flask was brought under a nitrogen atmosphere, after which dry pyridine (20 ml) and p-nitrophenylisocyanate (0.27 grams, 0.00016 mol) were added. After refluxing overnight, during which initially an almost clear solution was obtained, but later a suspension, the mixture was evaporated. The product is very poorly soluble. Recrystallisation from acetic acid followed by drying resulted in pure 2-(p-nitrophenyl)ureido-6-tridecyl-4-pyrimidone as a microcrystalline powder ¹H-NMR (CDCl₃, reflux): δ (ppm): 12.8 (s, 1H), 12.7 (s, 1H), 12.4 (s, 1H) 8.20 (d, 2H), 7.93 (d, 2H), 6.0 (s, 1H), 2.56 (t, 2H), 1.71 (m, 2H), 1.27 (m, 20H), 0.87 (t, 3H).

Example V

6-phenylisocytosine

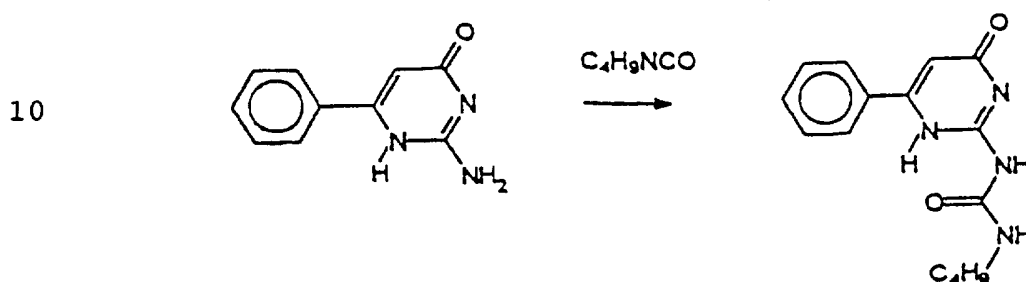


Guanidine carbonate (9.09 g, 0.05 mol) was weighed into a 2-neck flask (250 ml), after which the flask was brought under a nitrogen atmosphere. Next, dry ethanol (100 mol) was added, followed by ethyl benzoylacetate (commercial, 19.2 g, 0.10 mol). The mixture was refluxed overnight. After cooling to room temperature, 6-phenylisocytosine was removed through filtration, washed with ethanol, then water, then again ethanol and dried (12.02 g, 0.064 mol, 64%). ¹H-NMR (DMSO d₆): δ (ppm): 10.84 (br, 1H), 7.94 (m, 2H), 7.43 (m, 3H), 6.62 (br, 2H), 6.11 (s, 1H). ¹³C-NMR (DMSO d₆): (388K) δ(ppm): 162.8, 162.2, 155.2, 137.1, 128.9, 127.4, 125.9, 97.4. IR (KBr): ν (cm⁻¹): 3350, 3087, 2956, 1658,

1502, 1476, 1380. Element analysis: N 23.03% (calc. 22.45%), C 64.29% (calc. 64.16%), H 5.06% (calc. 4,85%). Melting point: 312°C.

5 Example VI

2-butylureido-6-phenyl-4-pyrimidone



15 6-phenylisocytosine (1.93 g, 0.010 mol) was weighed into a dry 2-neck flask (100 ml), after which the flask was brought under a nitrogen atmosphere. Next, pyridine (40 ml) was added, and butylisocyanate (1.69 ml, 0.015 mol). After 4 hours' refluxing, during which the

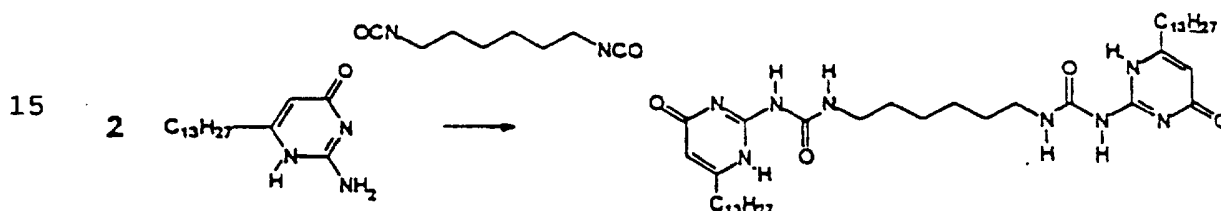
20 suspension gradually changed into a clear solution, the pyridine and the butylisocyanate were evaporated. The white powder was suspended in acetone and removed through filtration. To purify 2-butylureido-6-phenyl-4-pyrimidone, it was recrystallised from a 1:1 (v:v)

25 ethanol/chloroform mixture. The yield obtained after filtration and drying was 2.34 g (0.0082 mol, 82%). ¹H-NMR (CDCl₃): δ (ppm) (keto peaks): 13.9 (s, 1H), 12.1 (s, 1H), 10.2 (s, 1H), 7.7 (m, 2H), 7.5 (m, 3H), 6.4 (s, 1H), 3.3 (m, 2H), 1.7 (q, 2H), 1.5 (q, 2H), 0.9 (t, 3H). ¹³C-NMR (54°C) (CDCl₃): (enol and keto peaks) δ (ppm): 173.2, 157.0, 155.4, 148.8, 137.0, 131.1, 130.7, 129.6, 128.9, 126.9, 125.8, 104.4, 39.9, 31.6, 29.7, 20.2, 13.7. IR(KBr): (enol form): 3217, 31,37, 3029, 2958, 2873, 2587, 2511, 1658, 1614, 1557, 1444, 1327.

35 Both needles and plates could be obtained in crystallisation from chloroform by means of evaporation. The IR of the plates is identical to that

of the product obtained from ethanol-chloroform (enol form). In the keto form the needles are: ν (cm^{-1}) 3202, 3012, 2959, 2871, 1692, 1656, 1588, 1528, 1453, 1255. Element analysis: N 20.52% (calc. 19.57%), C 62.50% (calc. 62.92%), H 5.30% (calc. 6.34%). Melting point: enol powder: 245°C. Enol plate crystals 114°C phase transition, 245°C melting+sublimation, subsequently solidifying. Keto crystals: 85-120°C crystals splinter, 245°C melting+sublimation, subsequently solidifying.

10

Example VII2-(1,6-Hexadiyl)-6-tridecyl-4-pyrimidone

6-tridecylisocytosine (11.20 g, 0.04 mol) was weighed into a 2-neck flask (250 ml), after which the flask was brought under a nitrogen atmosphere. Pyridine (80 ml) and toluene (10 ml) were added to the flask. The mixture was heated to reflux temperature and a clear solution was obtained. Approx. 10 mol solvent was azeotropically removed through distillation. After cooling to room temperature hexane diisocyanate (3.33 g, 0.0198 mol) was added. The mixture was refluxed for 3 days, after which the addition of acetone resulted in the formation of a suspension, from which the product could be removed through filtration (93% yield). 2-(1,6-hexadiyl)-6-tridecyl-4-pyrimidone was purified by means of column chromatography with the aid of a flash silica column using as an eluant first 3% ethanol in chloroform, which was later gradually increased to 5% ethanol in chloroform. The substance showed tailing in the column, so only the initial fractions were pure. The fractions containing pure product were for the

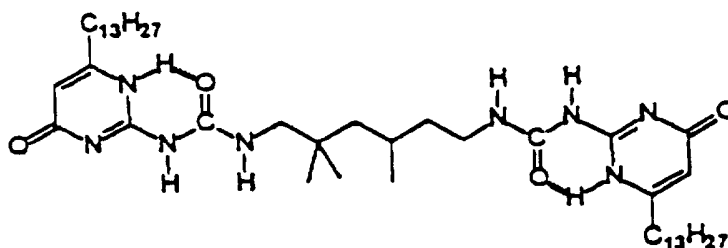
30

35

greater part evaporated and precipitated in acetone. Impure column fractions were once again separated in the same manner. Thorough drying resulted in a total overall yield of 66%. For optimum polymer properties it proved to be extremely important to have the substance in a very high purity. $^1\text{H-NMR}$ (CDCl_3): δ (ppm): 13.18 (s, 2H), 11.88 (s, 2H), 10.18 (s, 2H), 5.82 (s, 2H), 3.23 (s, 4H), 2.45 (t, 4H), 1.63 (d, 8H), 1.25 (m, 44H), 0.88 (t, 6H). $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm): 173.2, 156.6, 154.7, 152.4, 105.8, 40.0, 32.7, 31.9, 29.4, 29.3, 29.1 (overlapping peaks), 26.8, 22.7, 14.1. IR (KBr): ν (cm^{-1}): 3220, 3036, 2924, 2852, 2605, 1700, 1661, 1586, 1524, 1460, 1252. Element analysis: N 14.62% (calc. 14.84%), C 67.25% (calc. 66.81%), H 9.77% (calc. 9.88%). Melting point: from approx. 100°C 2-(1,6-hexadiyl)-6-tridecyl-4-pyrimidone became liquid but it did remain birefringent, after which it became isotropic at approx. 180°C. When cooled (slowly or quickly) the substance remained in a vitreous phase which did not crystallise (not even after a few weeks).

Example VIII

2-(1,6-trimethylhexadiyl)-6-tridecyl-4-pyrimidone



1.76 g (8.37 mmol) of trimethyl-1,6-diisocyanatohexane (a mixture of 2,4,4- and 2,2,4-) in 5 ml of dry pyridine was added to 4.82 g (16.4 mmol) of tridecylisocytosine, under an argon atmosphere. The reaction mixture was stirred for one night at 120°C.

- 18 -

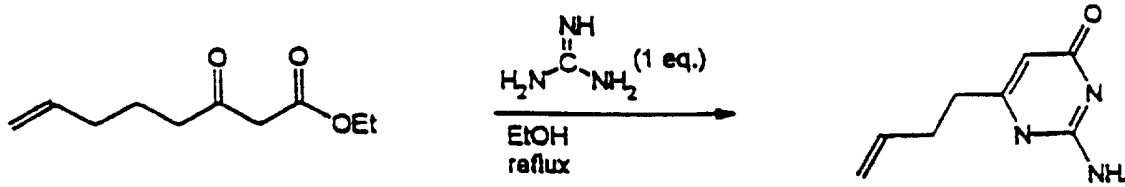
After it had cooled, the reaction mixture was precipitated in 250 ml of acetone. Next, the precipitate was purified via column chromatography (silica gel, 1% MeOH in chloroform) followed by
 5 recrystallisation from 300 ml of ethyl acetate. This resulted in the formation of 4.39 g (67%) of product, a highly viscous pale yellow oil.

$^1\text{H-NMR}$ (CDCl_3): δ (ppm): 12.99 (br s, 2H), 11.66 (br s, 2H), 9.90 (br s, 2H), 5.55 (s, 2H), 2.99 (s, 4H), 2.22
 10 (t, 4H), 1.41 (d, 8H), 1.06 (m, 53H), 0.67 (t, 6H). $^{13}\text{C-NMR}$ (CDCl_3): δ (ppm): 172.8, 156.4, 154.6, 152.1, 105.6, 35.7, 32.8, 32.5, 31.8, 29.4, 29.3, 29.0 (overlapping peaks), 27.1, 26.8, 25.0, 22.5, 22.2, 20.7, 14.0.

15

Example IX2-amino-6-(3-butenyl)-4-pyrimidone

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Guanidine carbonate (14.05 g; 0.078 mol; E. Merck AG) was weighed into a dry two-neck flask. Nitrogen gas was passed through the flask, after which dry ethanol (160
 30 ml) was added. The crude ethyl 3-oxo-6-heptenoate obtained in the previous step was added during the stirring. After refluxing for one night, the ethanol was partially evaporated and water (50 ml) was added. The white precipitate thus obtained was removed through
 35 filtration, washed with water, cold ethanol and cold acetone, and dried in a vacuum ($\eta = 38\%$).

$^1\text{H NMR}$ ($\text{DMSO } d_6$): δ 10.74 (s, 1H, NH), 6.54 (s, 2H, NH),

5.80 (m, 1H, $\underline{\text{H}}\text{C}=\text{CH}_2$), 5.40 (s, 1H, alkylidene), 5.01 (m, 2H, $\underline{\text{H}}_2\text{C}=\text{C}$), 2.3 (m, 2*2H, 2CH₂) ppm.

¹³C NMR (DMSO d₆): δ 167, 164.51, 155.84, 137.73, 115.23, 100.04, 35.63, 31.52 ppm.

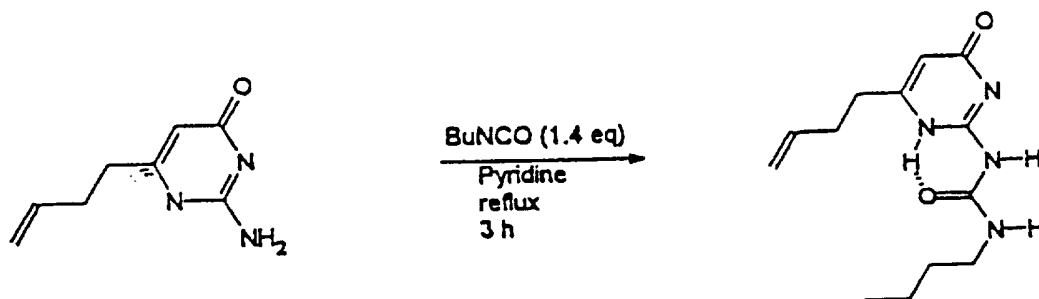
5 Element analysis: C₈H₁₁N₃O; C 57.29 % (calc. 58.17%), H 6.71% (6.71%), N 25.85 % (25.44%).

Example X

6-(3-butenyl)-2-butylureido-4-pyrimidone

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2-amino-6-(3-butenyl)4-pyrimidone (3 g; 18.16 mmol) was weighed into a dry two-neck flask and dissolved in dry pyridine (36 ml) with heating, in a nitrogen atmosphere. After everything had dissolved, n-butyl isocyanate (2.86 ml; 25.43 mmol; Aldrich) was added via a syringe. After three hours' stirring with reflux, the pyridine was evaporated. The product was isolated with the aid of crystallisation from ethanol (η = 87%).

30 ¹H-NMR (CDCl₃): δ 13.24 (s, 1H, NH), 11.87 (s, 1H, NH) 10.14 (s, 1H, NH), 5.84 (s, 1H, alkylidene), 5.79 (m, 1H, $-\underline{\text{H}}\text{C} = \text{CH}_2$), 5.09 (m, 2H, $\underline{\text{C}}\text{H}_2 = \text{CH}-$), 3.25 (m, 2H, CH₂, butyl), 2.58 (t, 2H, CH₂), 2.43 (m, 2H, CH₂) 1.59 (m, 2H, CH₂, butyl), 1.39 (m, 2H, CH₂, butyl), 0.96 (t, 3H, CH₃) ppm.

35

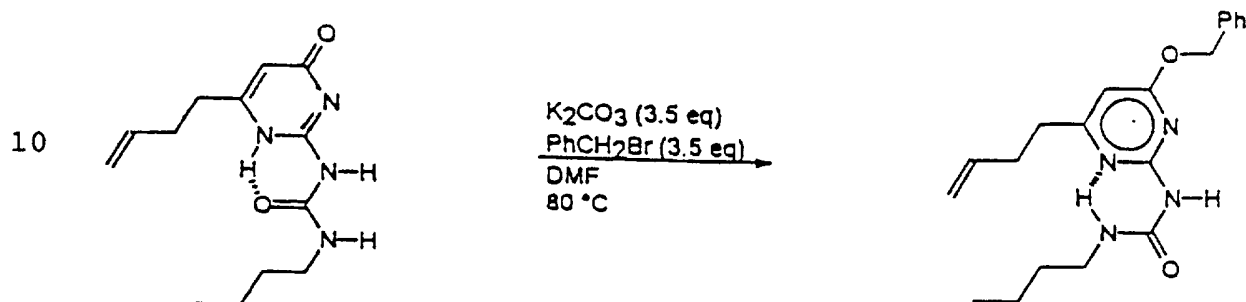
¹³C NMR (CDCl₃): δ 173.05, 156.56, 154.71, 151.38, 135.13, 116.94, 106.08, 39.78, 31.94, 31.53, 30.78,

20.15, 13.75 ppm.

Element analysis: $C_{13}H_{20}N_4O_2$; C 58.78% (calc. 59.07%), H 7.67% (7.63%), N 21.56% (21.20%).

5 Example XI

4-benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine



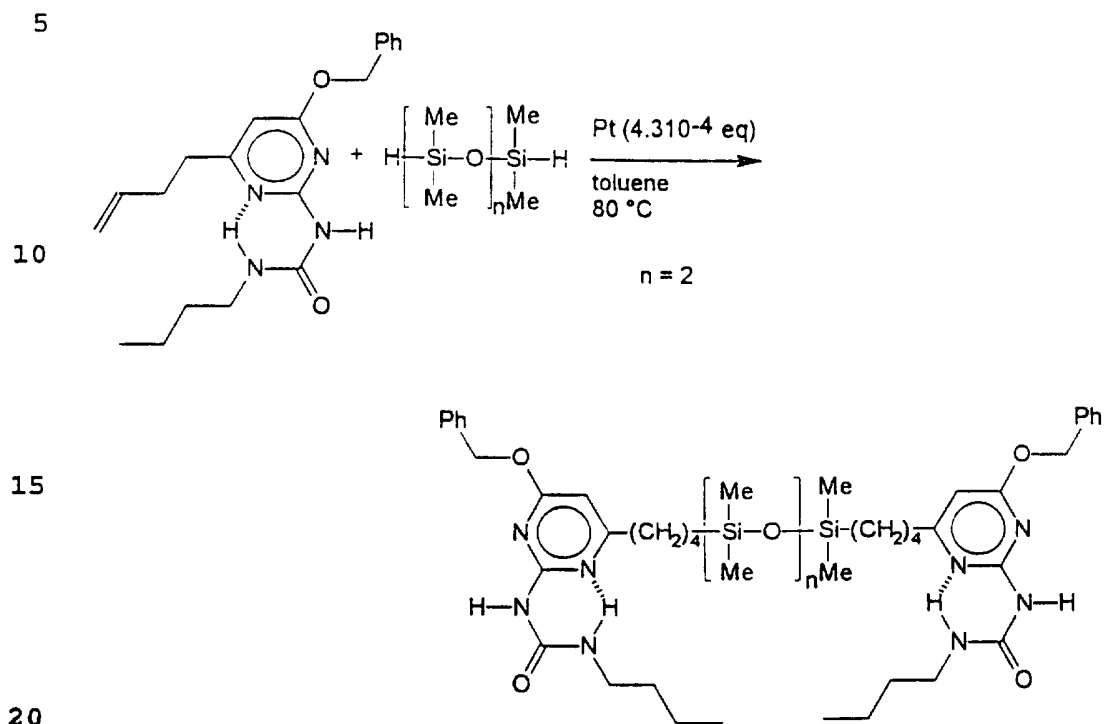
15 6-(3-butenyl)-2-butylureido-4-pyrimidone (1 g; 3.78 mmol) was weighed into a two-neck flask and dissolved in dry DMF (25 ml; Acros). Potassium carbonate (1.83 g, 13.24 mmol) was subsequently weighed and added. Benzyl bromide (1.58 ml; 13.24 mmol; Acros) was slowly added drop by drop via a syringe, with vigorous stirring. The whole was stirred at 80°C for one night. After that, a generous amount of acetone was added to the reaction mixture, after which potassium carbonate was removed through filtration and rinsed with acetone. Water was added to the filtrate until a precipitate formed. The product was subsequently crystallised from ethanol/water (3/1) and recrystallised from hexane (η = 78%).

30 1H NMR ($CDCl_3$): δ 9.21 (s, 1H, NH), 7.39 (m, 5H, Ph) 7.13 (s, 1H, NH), 6.22 (s, 1H, alkylidene), 5.84 (m, 1H, $-HC=CH_2$), 5.33 (s, 2H, CH_2 -Ph), 5.10 (m, 2H, $CH_2=CH-$), 3.37 (m, 2H, CH_2 , butyl), 2.70 (t, 2H, CH_2), 2.46 (m, 2H, CH_2), 1.59 (m, 2H, CH_2 , butyl), 1.45 (m, 2H, CH_2 , butyl), 0.96 (t, 3H, CH_3) ppm.

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Example XII

di[4-benzyloxy-6-butyl-2-butylureidopyrimidine]-
hexamethyltrisiloxane



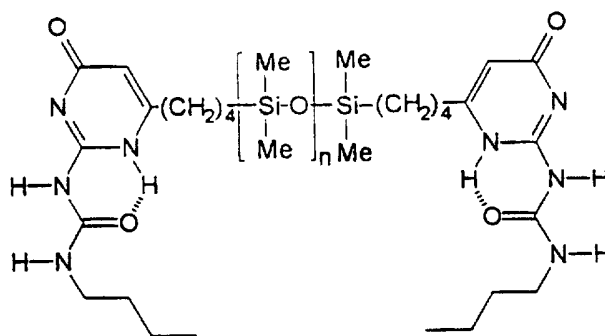
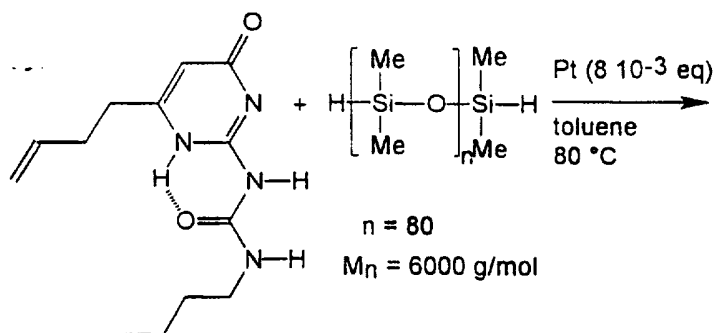
25 4-benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine
(0.177 g; 0.5 mmol) was weighed into a dry 10-ml
Schlenk vessel, after which the whole was introduced
into the glove box via an air lock.
Hexamethyltrisiloxane (0.052 g; 0.25 mmol) was weighed
30 into this. A solution of the platinum catalyst (2.1%-
2.4% in xylene, 1 μ l, 0.12 μ mol) in dry toluene was
prepared and added to the pyrimidine/siloxane mixture.
Dry toluene was finally added until the total amount of
toluene was approx. 1 ml. After one night's stirring at
35 80°C, toluene was removed through evaporation using a
Rotavapor. The product was ultimately isolated with the
aid of column chromatography (eluant: 7% THF in CHCl₃).

^1H NMR (CDCl_3): δ 9.30 (s, 2H, NH), 7.34 (m, 10H, Ph) 7.34 (s, 2H, NH), 6.19 (s, 2H, alkyldiene), 5.31 (s, 4H, CH_2 -Ph), 3.36 (m, 4H, CH_2 , butyl), 2.57 (m, 4H, CH_2), 1.68 (m, 4H, CH_2), 1.57 (m, 4H, CH_2 , butyl), 1.41 (m, 4H, CH_2 butyl), 1.41 (m, 4H, CH_2), 0.96 (t, 6H, CH_3), 0.56 (t, 4H, CH_2), 0.06 (s, 12H, Si- CH_3), -0.01 (s, 6H, Si- CH_3) ppm.

Example XIII

10 di[6-butyl-2-butylureido-4-pyrimidone]
polydimethylsiloxane

15



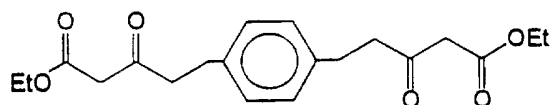
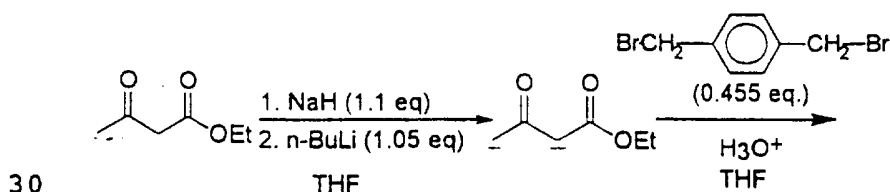
6-(3-butenyl)-2-butylureido-4-pyrimidone (0.0535 g; 0.2 mmol) was weighed into a dry 10-ml Schlenk vessel, after which the whole was introduced into the glove box via an air lock. Polydimethyltrisiloxane (PDMS) (0.168 g; 0.028 mmol; ABCR) was weighed into this. A solution of the platinum catalyst (platinum divinyl tetramethyldisiloxane complex, 2.1% - 2.4% in xylene; 2 μ l; 0.24 μ mol; ABCR) in dry toluene was prepared and added to the pyrimidine/PDMS mixture. Finally, dry
 10 toluene was added until the total amount of toluene was approx. 1 ml. After one night's stirring at 80°C toluene was removed through evaporation with the aid of the Rotavapor. The product was ultimately isolated with the aid of column chromatography (eluant: 7% THF in
 15 CHCl_3).

$^1\text{H NMR}$ (CDCl_3): δ 13.21 (s, 2H, NH), 11.89 (s, 2H, NH) 10.17 (s, 2H, NH), 5.84 (s, 2H, alkylidene), 3.25 (q, 4H, CH_2 , butyl), 2.47 (t, 4H, CH_2), 1.68 (m, 4H, CH_2), 1.59 (m, 4H, CH_2 , butyl), 1.41 (m, 4H, CH_2 , butyl), 1.41
 20 (m, 4H, CH_2), 0.94 (t, 6H, CH_3), 0.56 (t, 4H, CH_2), 0.06 (s, n*6H, Si- CH_3) ppm.

Example XIV

p-Di-(ethyl 3-oxo-5-pentanoate) benzene

25

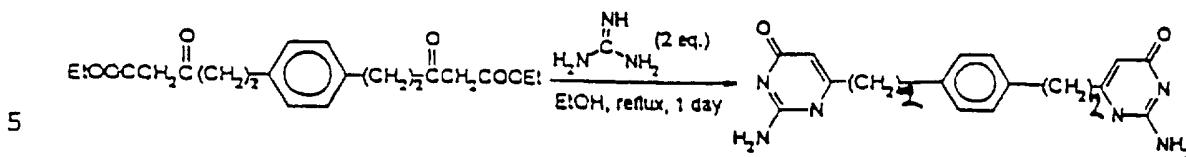


NaH (60 wt.%, 2.42 g; 60.5 mmol) was weighed into a three-neck flask fitted with a septum and a thermometer. Nitrogen gas was passed through and the whole was placed in an ice/salt bath. Dry THF (125 ml) was added and the suspension was vigorously stirred. At a temperature of 0°C, ethyl acetoacetate (6.96 g; 55 mmol; Merck-Schuchardt) was added drop by drop via a dry syringe. After 15 minutes' stirring at 0°C n-butyl lithium (1.6 M in hexane, 36.1 ml; 57.75 mol; Acros) was added, again drop by drop via a syringe, at 0°C. The whole was stirred for 15 minutes. In the meantime a solution was prepared of α,α' -dibromo-p-xylene (6.6 g; 25 mmol; Aldrich) in dry THF (66 ml), after which this solution was added to the dianion mixture via a dropping funnel, drop by drop, at 0°C. After 10 minutes' reaction the whole was quenched with the aid of a mixture of concentrated HCl (10 ml), water (25 ml) and ether (75 ml; technical grade). The water phase was separated from the organic phase. Next, the water layer was washed once with 100 ml of ether. The combined organic layers were then washed 4 times using 100 ml of water and once using a saturated NaCl solution. The ether layer was subsequently dried with the aid of sodium sulphate and filtered and the ether was evaporated via the Rotavapor (10.84 g). The crude product was however used as such in the synthesis of p-di-(2-amino-6-(ethyl)-4-pyrimidone) benzene.

^1H NMR (CDCl_3): δ 7.07 (s, 4H, Ar-H), 4.20 (q, 4H, OCH_2), 3.47 (s, 4H, CH_2), 2.87 (m, 4H, CH_2), 2.87 (m, 4H, CH_2), 1.28 (t, 6H, CH_3) ppm.

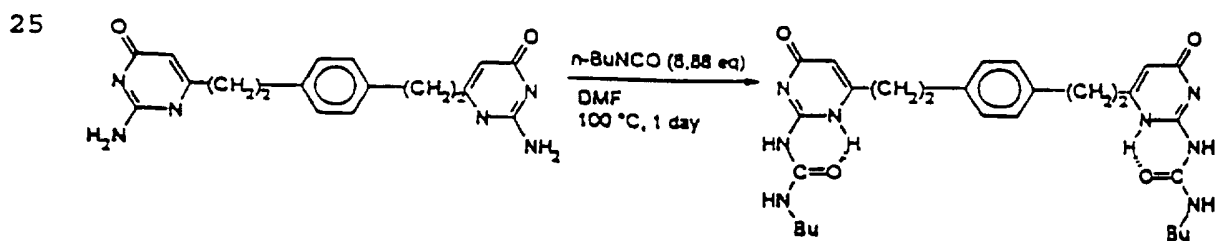
^{13}C NMR (CDCl_3): δ 201, 166.96, 138.30, 128.67, 61.24, 49.27, 44.33, 28.83, 13.96 ppm.

35

p-di-(2-amino-6-(ethyl)-4-pyrimidone) benzene

Guanidine carbonate (4.54 g; 25 mmol; E. Merck AG) was weighed into a dry two-neck flask. Nitrogen gas was passed through the flask, after which dry ethanol (50 ml) was added. The crude p-di-(ethyl 3-oxo-6-heptenoate) benzene obtained in the previous step was added during the stirring. After one night's refluxing, the solid substance was removed through filtration and washed with water, ethanol and acetone. The product was subsequently purified via crystallisation from acetic acid ($\eta_{\text{overall}} = 38\%$).

^1H NMR (DMSO d_6): δ 10.67 (s, 2H, NH), 7.11 (s, 4H, Ar-H), 6.51 (s, 4H, NH₂), 5.40 (s, 2H, alkylidene), 2.81 (t, 4H, Ar-CH₂) 2.50 (t, 4H, CH₂) ppm.

Example XV6-(3-butenyl)-2-butylureido-4-pyrimidone

p-di-(2-amino-6-ethyl-4-pyrimidone) benzene (1.76 g; 5 mmol) was weighed into a dry two-neck flask and mixed with dry DMF (25 ml), with heating, in a nitrogen atmosphere. n-butylisocyanate (5 ml; 44.4 mmol; Aldrich) was added to this suspension via a syringe. After 24 hours' stirring at 100°C a dash of acetone was added. The white precipitate was removed through filtration, washed with DMF and then with acetone, and

was finally dried in a vacuum ($\eta = 60\%$).

^1H NMR (DMSO d_6): δ 11.53 (s, 2H, NH), 9.67 (s, 2H, NH)
7.41 (s, 2H, NH), 7.12 (s, 4H, Ar-H) 5.76 (s, 2H,
5 alkyldiene), 3.14 (m, 4H, CH_2 , butyl), 2.84 (m, 4H,
 CH_2), 2.64 (t, 4H, CH_2), 1.46 (m, 4H, CH_2 , butyl), 1.30
(m, 4H, CH_2 , butyl), 0.89 (t, 6H, CH_3) ppm.

Example XVI

10 Determination of the viscosities of solutions of A in chloroform in the presence of B

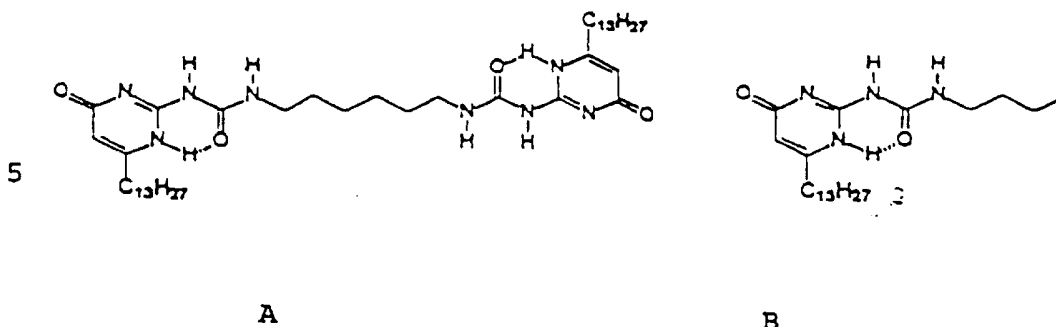
Solutions of A in chloroform have a substantially
increased viscosity. If this viscosity is caused by
linear linking of A by means of hydrogen bridges, the
15 viscosity will decrease when compound B is added,
because this compound can complex on one side only, and
prevents further growth of the chain by complexing with
A.

A stock solution containing about 40 mM of A
20 was prepared by dissolving 757 milligrams of A in 25
millilitres of chloroform. The viscosity of this
solution was determined by determining the time of
outflow in an Ubbelohde viscometer in a water bath that
was kept at a constant temperature of 20°C. From the
25 stock solution a second chloroform solution was
prepared, which contained the same amount of A plus a
precisely known amount of compound B. Amounts of this
second solution were subsequently added to the
viscometer portion by portion, so that solutions with a
30 constant concentration of A and an increasing series of
concentrations of the chain terminator B were obtained
(see the table). After each addition, the solution
obtained was mixed until it was homogeneous and the
viscosity was calculated by measuring the time of
35 outflow and using the necessary time correction factor.
Finally, the viscosity of the chloroform used was
measured so as to be able to determine relative

viscosities. The results of this experiment are presented in the following table:

Table: viscosity of a solution of A in chloroform at
5 25°C as a function of the added amount of B

	Conc. B conc. A	time of outflow (s)	viscosity η (Pa s)	relative viscosity
	0	274.7	4.04	7.48
10	0.00094	254.7	3.74	6.93
	0.00187	237.2	3.48	6.44
	0.00373	212.5	3.12	5.78
	0.00736	179.1	2.63	4.87
	0.0096	158.3	2.29	4.24
15	0.0143	144.9	2.12	3.93
	0.0191	129.0	1.93	3.57
	0.0385	103.0	1.53	2.83
	0.0746	84.8	1.238	2.29
	0.145	73.5	1.04	1.93
20	chloroform	45.6	0.54	1



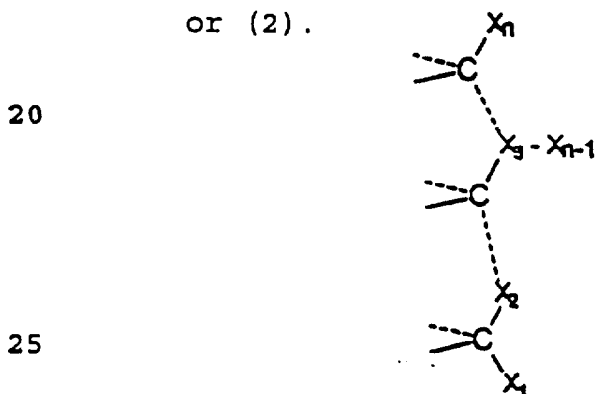
10 The experiment shows that a substantial reduction in
viscosity is observed even when only very small amounts
of B are added. The strength of the effect indicates
that molecules A in chloroform a) form linear polymer
chains and b) that these chains have an average length
15 of several hundreds of molecules.

Material properties of A

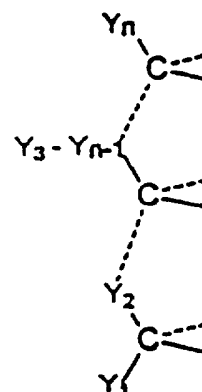
Compound A, obtained through precipitation of a
chloroform solution in acetone, is a white powder that
20 melts at 200°C. The viscosity of the melt is comparable
with that of glycerol at room temperature. During
cooling the viscosity gradually increases, until a
leathery, flexible substance forms. Long, highly
flexible threads can easily be drawn from the
25 supercooled melt above 100°C. Both the threads and the
bulk solid become noticeably brittle after a few
minutes at room temperature. After a few hours at room
temperature the material has become brittle. These
properties are typically those of a thermoplastic
30 polymer and are entirely uncommon in compounds with a
low molecular weight.

C L A I M S

1. Supramolecular polymer containing monomeric units
 5 that form H-bridges with one another,
 characterised in that the H-bridge-forming
 monomeric units in pairs form at least 4 H-bridges
 with one another.
2. Polymer according to any one of Claims 1, in which
 10 the H-bridge-forming monomeric units are self-
 complementary.
3. Polymer according to Claim 1 or Claim 2, in which
 the H-bridge-forming monomeric units constitute an
 essentially flat structure.
- 15 4. Polymer according to any one of Claims 1-3, in
 which the H-bridge-forming monomeric units contain
 a structural element having the general form (1)
 or (2).



(1)



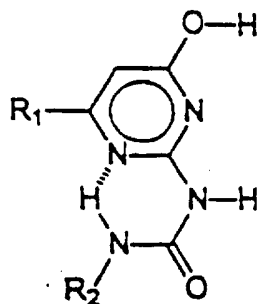
(2)

30 in which the C-X_i and C-Y_i linkages each represent
 a single or double bond, n is 4 or more and X₁...X_n
 represent donors or acceptors that form H-bridges
 with the H-bridge-forming monomeric unit
 containing a corresponding structural element 2
 linked to them, with Y_i representing an acceptor if
 35 X_i represents a donor, and vice versa.

5. Polymer according to Claim 4, in which the donors
 and acceptors are O, S or N atoms.

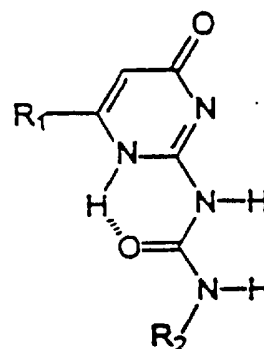
6. Polymer according to Claim 4 or Claim 5, in which $n=4$.
7. Polymer according to Claim 6, in which X_1 and X_2 are donors and acceptors, respectively, and X_3 and X_4 are acceptors and donors, respectively.
8. Polymer according to any one of Claims 4-7, containing an H-bridge-forming monomeric unit having the general formula (3.a) or (3.b)

10



(3.a)

15

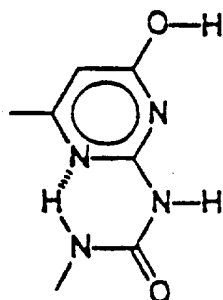


(3.b)

where $|||$ represents an H-bridge, R_1 a linking unit with a different monomeric unit and R_2 a side chain, or R_2 represents a linking unit and R_1 a side chain, or R_1 and R_2 both represent a linking unit.

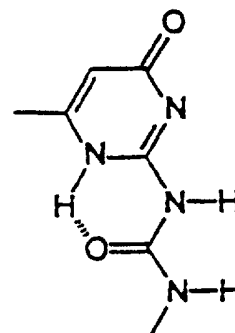
H-bridge-forming unit containing a structural element having the general formula

25



4.a

30



4.b

35

where $|||$ represents an H-bridge.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00535

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08G85/00 C08G83/00 C07D239/46 C08G77/54 C08G77/26
 C08G77/388

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 C07D

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

Electronic data base consulted during the international search (name of data base and, where 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	R. BUVET ET AL.: "INTERACTION HYDROGENE OU PONTS HYDROGENE" CHIMIE MACROMOLECULAIRE, vol. 1, 1956, PARIS, pages 21-22, XP002031480 see page 21 - page 22	1
A	CHEMICAL ABSTRACTS, vol. 85, no. 3, 1976 Columbus, Ohio, US; abstract no. 15348y, page 182; column 1; XP002031482 see abstract	6
A	& JP 07 622 823 A (NISSAN) 23 February 1976	6
	— — — — — — / — —	

Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "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 "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family
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Date of the actual completion of the international search <p style="text-align: center;">27 November 1997</p>	Date of mailing of the international search report <p style="text-align: center;">18/12/1997</p>
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx. 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center;">Francois, J</p>
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INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 97/00535

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>T.URBANSKI ET AL.: "POTENTIAL ANTIMALARIAL COMPOUNDS IX." JOURNAL OF MEDICINAL CHEMISTRY, vol. 10, no. 4, July 1967, WASHINGTON US, pages 521-525, XP002031481 see page 521 - page 525 -----</p>	6