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(54) Title: MONOMERS CAPABLE OF FORMING FOUR HYDROGEN BRIDGES AND SUPRAMOLECULAR POLYMERS FORMED BY COPOLYMERIZATION OF THESE MONOMERS WITH REGULAR MONOMERS

(57) Abstract: The invention relates to the synthesis of polymers containing self-complementary quadruple hydrogen groups by copolymerizing monomers containing a quadruple hydrogen bonding group with one or more monomers of choice. The resulting polymers show unique new characteristics due to the presence of additional physical interactions between the polymer chains that are based on multiple hydrogen bonding interactions (supramolecular interactions).

WO 2004/016598 A1

# MONOMERS CAPABLE OF FORMING FOUR HYDROGEN BRIDGES AND SUPRAMOLECULAR POLYMERS FORMED BY COPOLYMERIZATION OF THESE MONOMERS WITH REGULAR MONOMERS

## FIELD OF THE INVENTION

The invention relates to the synthesis of polymers containing self-complementary quadruple hydrogen groups by copolymerizing monomers containing a quadruple hydrogen bonding group with one or more monomers of choice. The resulting polymers show unique new characteristics due to the presence of additional physical interactions between the polymer chains that are based on multiple hydrogen bonding interactions (supramolecular interactions).

## BACKGROUND OF THE INVENTION

This invention relates to polymers containing units that are capable of forming H-bridges with each other leading to physical interactions between different polymer chains. The physical interactions originate from multiple hydrogen bonding interactions (supramolecular interactions) between self-complementary units containing at least four hydrogen bonds (units capable of forming at least four hydrogen bonds are in this application abbreviated as 4H-units or 4H-monomers and are used in this application as interchangeable terms) in a row. Sijbesma et al. (US 6.320.018; Science, 278, 1601) discloses such self-complementary units which are based on 2-ureido-4-pyrimidones. In Examples X the 4H-unit 6-(3-butenyl)-2-butylureido-4-pyrimidone is disclosed. Polymers obtained by polymerization of the carbon-carbon double bond moiety of this compound are, however, not disclosed.

Telechelic polymers have been modified with 4H-units (Folmer, B.J.B. et al., Adv. Mater. 2000, Vol. 12, 874; Hirschberg et al., Macromolecules 1999, Vol. 32, 2696). However, this has been performed after polymerization in a laborious post-modification process. Another drawback of these polymers containing 4H-units is that they only contain the 4H-unit coupled at the ends of the polymers. Consequently, the

number of end groups is therefore limited by the amount of end groups (normally 2), and the functional units are always located on the periphery of the polymer.

Polymers containing hydrogen bonding groups in the main chain synthesized via copolymerization of hydrogen bonding monomers have been obtained with hydrogen bonding units containing three H-bonds in a row (Lange F.M. et al., Macromolecules 1995, Vol 28, 782). However, only an alternating copolymer of styrene and maleimide can be used in this approach, and moreover, the H-bonding interactions between the polymers are much weaker than the H-bonding based on the 4H-units, obviously resulting in poorer material properties.

Polymers with quadruple H-bonding units in the main chain have been obtained by copolymerizing 4H-monomers in the main chain of a polyolefin (Coates, G.W. et al., Angew. Chem. Int. Ed., 2001, Vol. 40, 2153). However, complex chemistry has to be used to prepare and to polymerize the monomer and, due to the intrinsic sensitivity of the catalyst needed to obtain the polymer, severe limitations hinder the general use of this system and limits it to tailor-made polyolefin systems. For example, Coates et al. discloses the copolymerization of 1-hexene and a 6-hexenyl-2-ureido-4-pyrimidone derivative with a Ziegler-Natta type nickel based catalyst and diethylaluminum chloride as cocatalyst.

The present invention discloses a convenient synthesis and convenient copolymerization of monomers containing a 4H-unit with other widely available monomers. The present invention can be used for the preparation of a wide range of polymers with 4H hydrogen bonding units in order to provide these polymers with unique new material properties as a result of the incorporation of the 4H-units. These new material properties result from the reversible nature of H-bonding interactions between the polymer chains that allow reversible changing of the material properties by external stimuli like heat or dilution. Consequently, it becomes possible to prepare materials that combine the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds.

## SUMMARY OF THE INVENTION

According to the invention, the monomers comprise (a) a monomeric unit having a group that can be polymerized (or a monomeric unit having a polymerizable group), (b) a linking moiety and (c) a structural element capable of forming at least four hydrogen bridges, preferably four hydrogen bridges, wherein the monomer has the general structure:

(a) - (b) - (c)

## DETAILED DESCRIPTION OF THE INVENTION

### Description of the monomer containing the 4H-unit

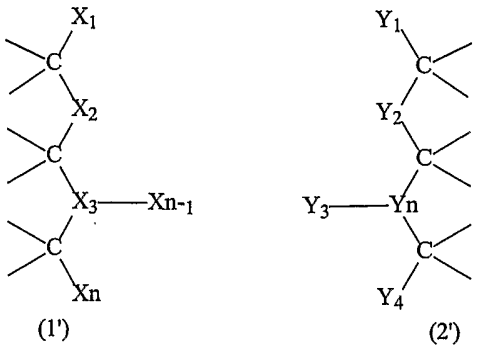
The monomer containing the 4H-unit comprises a group that can be polymerized, a linker and a 4H-unit. In particular, the group that can be polymerized is linked to a 4H-unit via a linker as is shown below in schematic form.


According to the invention, the monomers comprise (a) a monomeric unit having a group that can be polymerized (i.e. a monomeric unit having a polymerizable group), (b) a linking moiety and (c) a structural element capable of forming at least four hydrogen bridges, preferably four hydrogen bridges, wherein the monomer has the general structure:

(a) - (b) - (c)

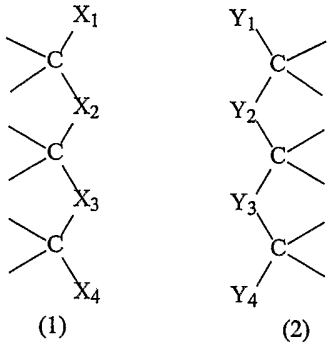
Preferably, (a) comprises monomeric units having an ethylenically unsaturated group or an ion-polymerizable group. Most preferably, group (a) comprises monomeric units having an ethylenically unsaturated group.

In general, the structural element that is capable of forming at least four hydrogen bridges has the general form (1') or (2'):




(1') (2')

If the structural element (c) is capable of forming four hydrogen bridges which is preferred according to the invention, the structural element (c) has preferably the general form (1) or (2):




(1) (2)

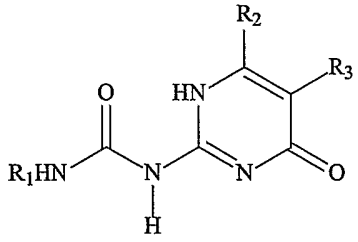
In all general forms shown above the C-$X_i$ and C-$Y_i$ linkages each represent a single or double bond, n is 4 or more and $X_1$ ... $X_n$ represent donors or acceptors that form hydrogen bridges with the H-bridge-forming unit containing a corresponding structural element (2) linked to them, with $X_i$ representing a donor and $Y_i$ an acceptor or vice versa. Properties of the structural element having general forms (1'), (2'), (1) or (2) are disclosed in US 6.320.018 which for the US practice is incorporated herein by reference.

The structural elements (c) have at least four donors or acceptors, preferably four donors or acceptors, so that they can in pairs form at least four hydrogen bridges with one another. Preferably the structural elements (c) have at least two successive donors, followed by at least two acceptors, preferably two successive donors followed by two

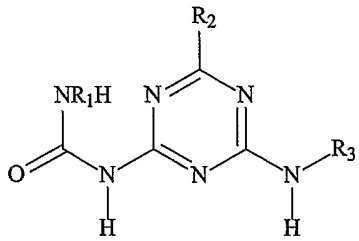
successive acceptors, preferably structural elements according to general form (1') or more preferably (1) with n=4, in which $X_1$ and $X_2$ both represent a donor and an acceptor, respectively, and $X_3$ and $X_4$ both an acceptor and a donor, respectively. According to the invention, the donors and acceptors are preferably O, S, and N atoms.

Molecules that can be used to construct the structural element (c) are nitrogen containing compounds that are reacted with isocyanates or thioisocyanates, or that are activated and reacted with primary amines, to obtain a urea moiety that is part of the quadruple hydrogen bonding site. The nitrogen containing compound is preferably an isocytosine derivative (i.e. a 2-amino-4-thymidone derivative) or a triazine derivative, or a tautomer of these derivatives. More preferably, the nitrogen containing compound is an isocytosine having an alkyl or oligoethylene glycol group in the 6-position, most preferably methyl, or ethylhexyl. The isocyanates or the thioisocyanates can be monofunctional isocyanates or monofunctional thioisocyanates or bifuntional diisocyanates or bifunctional thioisocyanates (for example alkyl or aryl (di)(thio)isocyanate(s)).

A particularly suitable structural element (c) according to the invention are the compounds shown below having general formulae (3) or (4), and tautomers thereof:




(3)




(4)

The structural element (c) according to formulae (3) or (4), respectively, is preferably bonded to the linking moiety (b) at $R_1$, $R_2$ or $R_3$ (so that $R_1$, $R_2$ or $R_3$ represent a direct bond) with the other R groups representing a random side chain or are hydrogen atoms. More preferably, the structural element (c) is bonded to the linking moiety (b) at $R_1$ (so that $R_1$ represents a direct bond) whereas $R_2$ and $R_3$ are a random side chain or are hydrogen atoms. Most preferably, $R_2$ is a random side chain and $R_3$ a hydrogen atom, wherein the random side chain is an alkyl or oligoethylene glycol group in the 6-position, most preferably methyl, or ethylhexyl.

The linking moiety (b) may be all kinds of shorter or longer chains, for example saturated or unsaturated, branched, cyclic or linear alkyl chains, siloxane chains, ester chains, ether chains and any chain of atoms used in traditional polymer chemistry, whether or not substituted with functional groups such as esters, ethers, ureas or urethanes. Preferably, the linking moiety (b) is a $C_1$-$C_{20}$ straight chain or branched alkylene, arylene, alkarylene or arylalkylene group, more preferably a $C_2$-$C_{10}$ straight chain or branched alkylene, arylene, alkarylene or arylalkylene group, wherein the alkylene, arylene, alkarylene or arylalkylene group may be substituted with other groups or may contain cyclic groups as substituent or in the main chain. Examples of such groups are methylene, ethylene, propylene, tetramethylene, pentamethylene, hexamethylene heptamethylene, octamethylene, nonamethylene, 1,6-bis(ethylene)cyclohexane, 1,6-bismethylene benzene, etc. The alkylene, arylene, alkarylene or arylalkylene groups may be interrupted by heteroatoms, in particular heteroatoms selected from the group of oxygen, nitrogen, and sulphur. The linking moiety (b) that links the monomeric unit having a polymerizable group (a) to structural element (c) is derived from a compound that must have at least two functional groups, e.g. hydroxy, carboxylate, carboxylic ester, ester halide, isocyanate, thioisocyanate, primary amine, secondary amine, or halogen functions. These functional groups are preferably present as end groups. According to the invention, such preferred compounds from which the linking moieties (b) are derived are preferably those having isocyanate or thioisocyanate end groups, more preferably isocyanate end groups. Most preferably, these compounds are diisocyanates or dithioisocyanates, in particular diisocyanates. Examples of suitable diisocyanates that can be used in this invention are:

1,4-diisocyanato-4-methyl-pentane,

1,6-diisocyanato-2,2,4-trimethylhexane,

1,6-diisocyanato-2,4,4-trimethylhexane,

1,5-diisocyanato-5-methylhexane,

3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate,

1,6-diisocyanato-6-methyl-heptane,

1,5-diisocyanato-2,2,5-trimethylhexane,

1,7-diisocyanato-3,7-dimethyloctane,

1-isocyanato-1-methyl-4-(4-isocyanatobut-2-yl)-cyclohexane,

1-isocyanato-1,2,2-trimethyl-3-(2-isocyanato-ethyl)-cyclopentane,

1-isocyanato-1,4-dimethyl-4-isocyanatomethyl-cyclohexane,
1-isocyanato-1,3-dimethyl-3-isocyanatomethyl-cyclohexane,
1-isocyanatol-n-butyl-3-(4-isocyanatobut-1-yl)-cyclopentane.
1-isocyanato-1,2-dimethyl-3-ethyl-3-isocyanatomethyl-cyclopentane,
3(4)-isocyanatomethyl-1-methylcyclohexyl isocyanate (IMCI),
toluene diisocyanate (TDI),
methylene diphenyl diisocyanate (MDI),
methylene dicyclohexane 4,4-diisocyanate,
isophorone diisocyanate (IPDI), hexane diisocyanate (HDI).

Examples of suitable thioisocyanates are the dithioisocyanate derivatives of the compounds exemplified above for suitable dithiocyanates.

Preferably, the diisocyanate is IPDI, HDI, MDI, TDI or methylene dicyclohexane 4,4-diisocyanate and their thioisocyanate counterparts. According to the invention, however, the diisocyanates are more preferably used than dithioisocyanates.

The monomeric unit having a polymerizable group (a) can be any monomeric unit having a polymerizable group. The monomeric unit having a polymerizable group (a) comprises preferably monomeric units having an ethylenically unsaturated group or an ion-polymerizable group and most preferably the monomeric unit having a polymerizable group comprises a monomeric unit having an ethylenically unsaturated group, i.e. a group derived from monomers having a carbon carbon double bond. According to a preferred embodiment of the invention, the monomeric unit having a polymerizable group has at least one functional group such as hydroxy, carboxylic acid, carboxylic ester, ester halide, isocyanate, thioisocyanate, primary amine, secondary amine or halogen groups. According to a more preferred embodiment of the invention, the monomeric unit having a polymerizable group is derived from acrylates, methacrylates, acrylamides, methacrylamides, styrenes, vinyl-pyridines, other vinyl monomers, lactones, other cyclic esters, lactams, cyclic ethers and cyclic siloxanes. According to the most preferred embodiment of the invention, the monomeric unit having a polymerizable group is derived from acrylates, methacrylates and vinyl esters, most preferably vinyl acetates. Examples of compounds from the monomeric units having a polymerizable group that are in particular useful in carrying out the invention are: 2-hydroxyethyl acrylate, 2-hydroxy-propyl acrylate, 2,3-dihydroxypropyl acrylate, poly(ethylene glycol) acrylate, acrylamide, N-hydroxymethyl acrylamide, 2-

hydroxyethyl methacrylate, 2-hydroxy-propyl methacrylate, 2,3-dihydroxypropyl methacrylate, poly(ethylene glycol) methacrylate, N,N-dimethylaminoethylmethacrylate, N-hydroxymethyl methacrylamide, vinylacetate, 4-vinyl phenol, 4-vinyl aniline, 4-hydroxymethyl-styrene, 4-aminomethyl-styrene, 4(2-hydroxyethyl)-ε–caprolactone, 4(4-hydroxyphenyl)-ε–caprolactone, and 2,3-epoxy-1-propanol.

According to the invention, the monomers are preferably prepared by the following methods.

According to a first method, the monomeric unit having a polymerizable group is reacted in a first step with the compound that must have at least two functional groups. In a subsequent step, the product obtained in the first step is reacted with the nitrogen containing compound. Suitable and preferred structures of the monomeric unit having a polymerizable group, the compound that must have at least two functional groups and the nitrogen containing compound are described above.

According to a second method, the nitrogen containing compound is reacted in a first step with the compound that must have at least two functional groups. In a subsequent step, the product obtained in the first step is reacted with the monomeric unit having a polymerizable group.

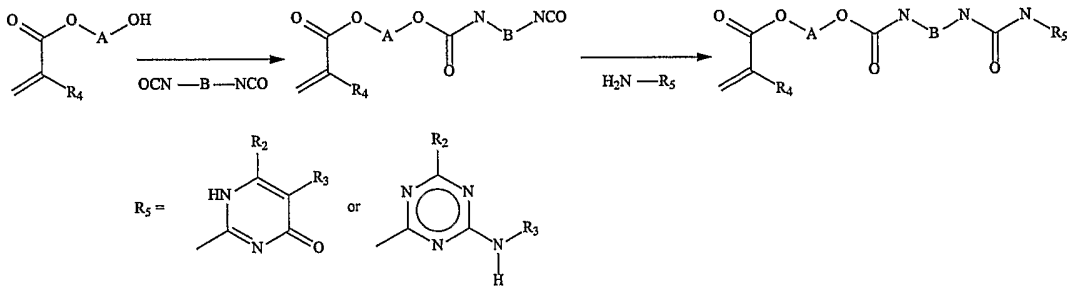
According to a third method, the nitrogen containing compound is reacted directly with the monomeric unit having a polymerizable group wherein the monomeric unit is able to form a urea linkage between both reactants.

According to these methods, the monomeric unit having a polymerizable group is most preferably selected from the group of monomeric units having an ethylenically unsaturated group, in particular monomers having a carbon carbon double bond, wherein the monomeric unit having a polymerizable group has preferably at least one functional group, wherein the functional group is selected from the group of hydroxy, carboxylic acid, carboxylic ester, ester halide, isocyanate, thioisocyanate, primary amine, secondary amine or halogen groups. More preferably, the monomeric unit having a polymerizable group is selected from the group of acrylates, methacrylates, acrylamides, methacrylamides, styrenes, vinyl-pyridines, other vinyl monomers, lactones, other cyclic esters, lactams, cyclic ethers and cyclic siloxanes having a functional group selected from hydroxy, carboxylic acid, carboxylic ester, isocyanate, thioisocyanate, primary amine, secondary amine or halogen groups. Even more

preferably, the monomeric unit having a polymerizable group is selected from the group of acrylates, methacrylates and vinyl esters, in particular vinyl acetates, said acrylates, methacrylates and vinyl esters having preferably a functional group selected from hydroxy, carboxylic acid, carboxylic ester, ester halide, isocyanate, thioisocyanate, primary amine, secondary amine or halogen groups.

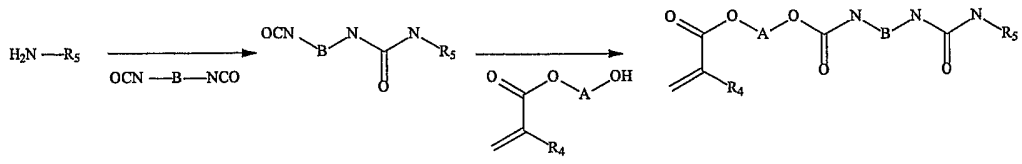
Preferred embodiments of the methods for the preparation of the monomers are shown below in Schemes 1 - 3.

Scheme 1

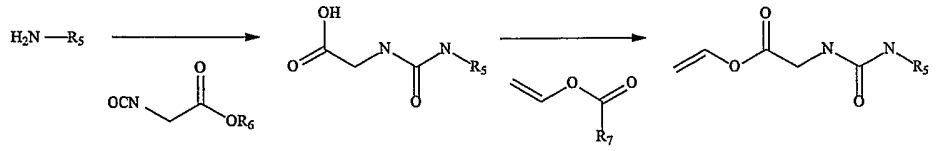



wherein $R_2$ and $R_3$ are as defined above, $R_4$ is hydrogen or methyl, A is a chain, preferably an oligomethylene chain or an oligoethylene glycol chain (as will be appreciated by the person skilled in the art, A may be absent so that the monomeric unit having a polymerizable group has a carboxylic group as functional group) and B is the chain of the linking moiety (b) described above.

Scheme 2



Scheme 3



In Scheme 3 $R_6$ and $R_7$ represent each independently a $C_1$-$C_6$ alkyl group, wherein $R_7$ is preferably methyl.

**Description of the co-polymerization and of the polymer**

The polymers presented in this invention are obtained by co-polymerizing the monomer containing the 4H-unit with one or more, optionally different comonomers that can be from the same family or from a different family of monomers. These comonomers are preferably selected from the group of: acrylic acid; $C_1$-$C_{30}$ branched or linear alkyl esters of acrylic acid; methacrylic acid; $C_1$-$C_{30}$ branched or linear alkyl esters of methacrylic acid; acrylamides or methacrylamides wherein the amide group may be substituted with one or two $C_1$-$C_{30}$ branched or linear alkyl groups; vinyl esters, preferably vinyl acetates; other compounds having a vinyl group wherein said compounds are preferably selected from pyrrolidones, imidazoles, pyridines, caprolactams, piperidones, benzene and derivatives thereof; $C_4$-$C_{20}$ alkadienes; lactones; lactams; and saturated or unsaturated heterocyclic compounds containing one to five oxygen atoms. Examples of suitable comonomers are acrylic acid, methyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, 2-hydroxyethyl acrylate, N,N-dimethylacrylamide, N-isopropylacrylamide, methacrylic acid, methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, 2-ethylhexyl methacrylate, lauryl methacrylate, 2-hydroxy-ethyl methacrylate,, vinylacetate, N-vinylpyrrolidinone, 2-vinylpyridine-1-oxide, N-vinyl imidazole, N-vinyl pyridine, N-vinylcaprolactam, N-vinyl-2-piperidone, acrylonitrile, styrene, butadiene, isoprene, caprolacton, butyrolacton, caprolactam, ethyleenoxide, propyleneoxide, tetrahydrofuran, 3,6-dimethyl-1,4-dioxane-2,5-dione, 1,4-dioxane-2,5-dione.

The copolymerizations may be of any type (for example, bulk, dispersion, solution, emulsion, suspension or inverse phase emulsion) and of any mechanism (for example, radical polymerization, condensation polymerization, transition metal catalyzed polymerization, enzymatic polymerization, or ring opening polymerization).

The copolymer backbone acquired may be of any type (linear, branched, star, hyperbranched, dendritic, comb-like or the like).

The product copolymer may be of any structure. For example random, regular, tapered or block copolymer structures are allowed.

According to the invention, the molecular weights of the polymers are preferably not too high. A preferred number average molecular weight range is 500 - 20000.

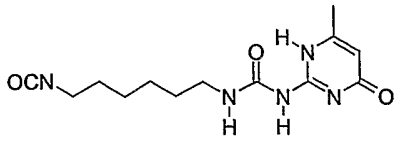
The copolymers according to the invention are in particular suitable for applications related to personal care (hair preparations, skin cosmetics and laundry aids), surface coatings (leather, textile, optical fibers, paper and paint formulations), imaging technologies (printing, stereolithography, photography and lithography), biomedical applications (materials for controlled release of drugs and materials for tissue-engineering, tablet formulation), adhesive and sealing compositions, and thickening agent and binders.

## EXAMPLES

The following non-limiting examples further illustrate the preferred embodiments of the invention. When not specifically mentioned, chemicals are obtained from Aldrich.

### Synthesis of building blocks

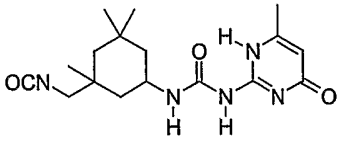
*Example 1: synthesis of isocyanate I*

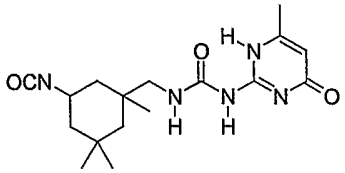



1,6-Hexyldiisocyanate (650 g) and methyl isocytosine (or 2-amino-4-hydroxy-6-methyl-pyrimidine, 65.1 g) were suspended in a 2-liter flask. The mixture was stirred

overnight at 100 °C under an argon atmosphere. After cooling to room temperature, a liter of pentane was added to the suspension, while stirring was continued. The product was filtered, washed with pentane and dried in vacuum. A white powder was obtained. $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 11.8 (1H), 10.1 (1H), 5.8 (1H), 3.3 (4H), 2.1 (3H), 1.6 (4H), 1.4 (4H). FT-IR (neat): ν 2935, 2281, 1698, 1668, 1582, 1524, 1256.

*Example 2: synthesis of isocyanate II*

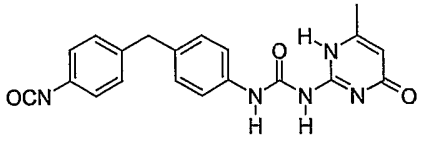



Methyl isocytosine (5.2 g) was added to isophoronediisocyanate (IPDI, 50 mL) and subsequently stirred at 90 °C under an argon atmosphere for 3 days. The resulting clear solution was precipitated in heptane. The white gom was collected, heated in 150 mL heptane, cooled on ice, and filtered. The same procedure was repeated once more with the white residue, resulting in a white powder. $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 12.0 (1H), 10.1 (1H), 5.9 (1H), 4.1-3.1 (3H), 2.1 (3H), 2.0-0.9 (15H). FT-IR (neat): ν ($cm^{-1}$) 2954, 2255, 1696, 1662, 1582, 1524, 1247.

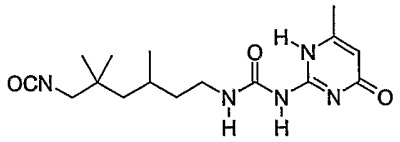
The product exists in four different isomers: the two regio-isomers depicted above are both present in cis and trans configuration. For reasons of clarity, only one isomer is depicted in the following schemes, although all four isomers are present.

*Example 3: synthesis of isocyanate III*



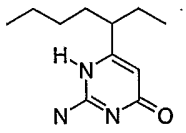

Methyl isocytosine (2.0 g) was added to 4,4'-methylenebis(phenylisocyanate) (MDI, 8.1 g) dissolved in 35 mL THF and subsequently stirred at an oil bath temperature of 75 °C under an argon atmosphere. After 4 hours, 40 mL chloroform was added and the white precipitate was separated by filtration and washed with chloroform. $^1$H NMR (400 MHz, DMSO-d6): δ 10.0 (1H), 8.6 (1H), 7.4 (5H), 7.2 (4H), 5.8 (1H), 3.8 (2H), 2.1 (3H). FT-IR (neat): ν ($cm^{-1}$) 3329, 2954, 2257, 1699, 1658, 1578, 1508, 1244.

*Example 4: synthesis of isocyanate IV*



A suspension of methyl isocytosine (2 g) and trimethyl-1,6-hexyldiisocyanate (a mixture of 2,2,4-trimethyl and 2,4,4-trimethyl isomers; 24 g) was stirred and heated for 21 hours at an oil bath temperature of 100 °C. The mixture was kept under an argon atmosphere. The reaction mixture was cooled down to room temperature and pentane was added to induce precipitation. The suspension was filtrated over a glass filter and the gummy residue was stirred and heated again in pentane. Cooling, filtration and drying gave a white powder. $^1$H NMR (300 MHz, $CDCl_3$): δ = 13.1 (1H), 11.7 (1H), 10.1 (1H), 5.8 (1H), 3.4–3.0 (4H), 2.2 (3H), 1.8 (1H), 1.6 (2H), 1.3 (1H), 1.1 (1H), 1.05-0.95 (9H). FT-IR (neat): υ ($cm^{-1}$) 2933, 2260, 1693, 1647, 1580, 1518, 1248. The product exists in eight isomers, as both trimethyl hexyldiisocyanates are chiral and can react at both isocyanate positions. For reasons of clarity, only one isomer is depicted (without assignment of stereocenter), although all isomers are present.

*Example 5: synthesis of 6-(1-ethylpentyl)-isocytosine*

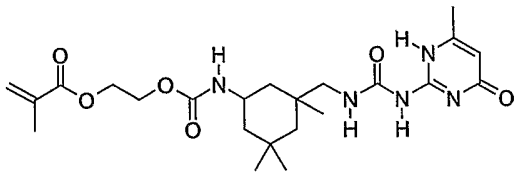


Potassium ethyl malonate (150 g) and acetonitrile (1.4 L) were stirred in a flask and brought to a temperature of 10-15 °C. Triethylamine (132 mL) was added drop wise, while keeping the mixture under an argon atmosphere. Dried $MgCl_2$ (101.6 g) was added and the suspension was stirred for 2 hours at room temperature. Thereafter, the suspension was cooled to 0 °C and 2-ethylhexanoyl chloride (74 mL) was added drop wise, and the mixture was allowed to warm up to room temperature and was stirred overnight. The acetonitrile was removed by evaporation, 400 mL toluene was added and evaporated, 700 mL of toluene was added and the mixture was cooled to 10 °C. An aqueous HCl solution was added slowly, and the organic layer was separated, washed with an HCl solution and then with a bicarbonate solution. The organic layer was dried

with $Na_2SO_4$ and concentrated to give the β-ketoester as a liquid. The β-ketoester (50 g) and guanidine carbonate (49.8 g) were boiled in ethanol (300 mL) for two days using a Soxhlett set-up with molsieves in the thimble. The suspension was filtered, ethanol was evaporated and the product was dissolved in chloroform. After washing with a bicarbonate solution, the organic layer was dried with $MgSO_4$, concentrated and dropped into an excess of pentane to yield a white powder. $^1H$ NMR (400 MHz, $CDCl_3$): δ 11.6-10.6 (1H), 7.6-6.6 (2H), 5.6 (1H), 2.2 (1H), 1.5 (4H), 1.2 (4H), 0.8 (6H). FT-IR (neat): ν 3322, 3152, 2929, 2860, 1635, 1463, 1378, 1582, 1524.

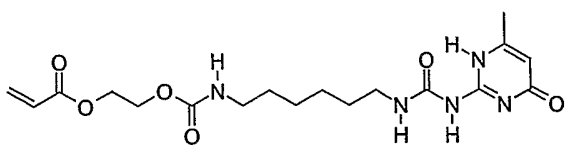
**Synthesis of 4H hydrogen bonding unit containing monomers**

*Example 6: monomer 1, a 4H hydrogen bonding unit containing methacrylate monomer*



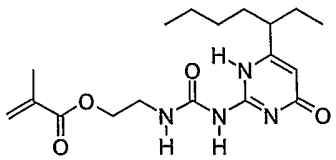
Isocyanate II (28 g) was dissolved in chloroform (0.5 L), and thereafter hydroxy ethyl methacrylate (HEMA, 9.6 mL) and 8 drops of dibutyl tin dilaurate (DBTDL) were added. The mixture was stirred at an oil bath temperature of 90 °C for 4 hours, and was then cooled and filtered. The filtrate was concentrated and dropped into an excess of diethylether. The precipitate was collected by filtration, and was washed with diethylether. Drying in vacuo gave a solid product. $^1H$ NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 11.8 (1H), 10.1 (1H), 6.1 (1H), 5.8 (1H), 5.6 (1H), 5.0 (1H), 4.3 (4H), 4.1-3.6 (1H), 3.1-2.9 (2H), 2.1 (3H), 2.0 (3H), 1.8-1.5 (2H), 1.4-0.8 (13H). FT-IR (neat): ν 3212, 2954, 1697, 1660, 1572, 1520, 1242, 1165.

*Example 7: monomer 2, a 4H hydrogen bonding unit containing acrylate monomer*



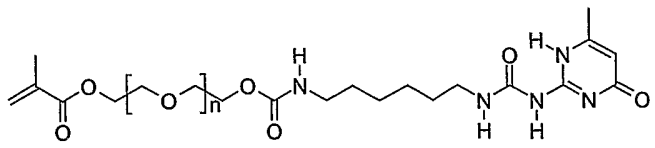
Isocyanate I (46 g) was suspended in chloroform (1 L), and thereafter hydroxy ethyl acrylate (HEA, 36 mL) and 10 drops of dibutyl tin dilaurate (DBTDL) were added. The mixture was stirred at an oil bath temperature of 90 °C for 4 hours, and was then cooled and filtered. The filtrate was concentrated and an excess of diethylether was added. The white precipitate was collected by filtration, and was washed with diethylether. Drying in vacuo gave a white solid product. $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 11.8 (1H), 10.1 (1H), 6.5 (1H), 6.2 (1H), 5.9 (2H), 5.1 (1H), 4.4 (4H), 3.3 (2H), 3.2 (2H), 2.1 (3H), 1.7-1.3 (8H). FT-IR (neat): ν 3307, 2928, 1725, 1702, 1682, 1664, 1584, 1548, 1258, 1192.

*Example 8: monomer **3**, a 4H hydrogen bonding unit containing methacrylate monomer*



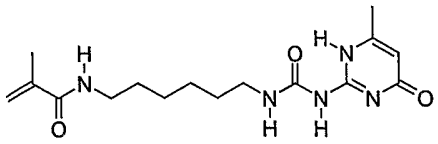
2-Isocyanatoethyl methacrylate (7.0 mL) was added to a solution of 6-(1-ethylpentyl)-isocytosine (13.4 g) in dry pyridine (150 mL). The reaction mixture was stirred under an argon atmosphere at 80 °C for 4 hrs. The product was worked-up by evaporation of the solvent, and subsequent filtration over silica using chloroform/methanol (4%). Silica column chromatography using ethyl acetate/hexane yielded a light yellowish waxy solid. $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 12.0 (1H), 10.5 (1H), 6.2 (1H), 5.8 (1H), 5.6 (1H), 4.3 (2H), 3.6 (2H), 2.3 (1H), 1.9 (3H), 1.8-1.5 (4H), 1.4-1.2 (4H), 0.9 (6H). FT-IR (neat): ν 2959, 2930, 1720, 1697, 1645, 1582, 1555, 1525, 1462, 1254, 1160.

*Example 9: monomer **4**, a 4H hydrogen bonding unit containing methacrylate monomer*



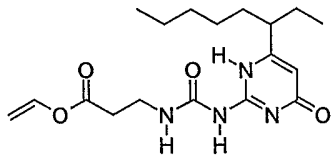
PEG-MA alcohol (with an average molecular weight Mn of 360; 2.2 g), isocyanate I (1.8 g) and a few drops of DBTDL were boiled overnight in chloroform. Hexane was added to cause precipitation. The product was isolated by filtration, washing with hexane and with diethyl ether. $^1$H NMR (400 MHz, DMSO-$d_6$): δ 7.5 (1H), 7.2 (1H), 6.0 (1H), 5.7 (1H), 5.6 (1H), 4.2 (2H), 4.0 (2H), 3.7 (2H), 3.6-3.4 (15H-20H), 3.1 (2H), 2.9 (2H), 2.1 (3H), 1.9 (3H), 1.4 (4H), 1.2 (4H).

*Example 10: monomer **5**, a 4H hydrogen bonding unit containing acrylamide monomer*



Isocyanate I (1 g) was dissolved in 5 mL of acrylic acid and heated to 60 °C. The mixture was stirred under an argon atmosphere. Copper(II)acetate (8 mg) was added and heating at 60 °C was maintained for 2 hours. The product was obtained by precipitation of the reaction mixture into diethylether. Then the solid was filtered, dissolved in chloroform and washed with a bicarbonate solution. Drying with $Na_2SO_4$ and column chromatography using chloroform with 10% methanol gave a white powder. $^1$H NMR (400 MHz, $CDCl_3/CD_3OD$): δ 7.4 (1H), 6.3-6.1 (2H), 5.8 (1H), 5.6 (1H), 3.3-3.2 (4H), 2.1 (3H), 1.7-1.2 (8H). FT-IR (neat): ν 3278, 2935, 1699, 1665, 1652, 1582, 1525.

*Example 11: monomer **6**, a 4H hydrogen bonding unit containing vinyl-ester monomer*

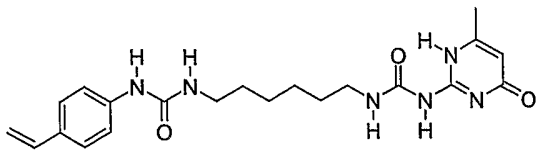


6-(1-Ethylpentyl)-isocytosine (3.5 g) was dissolved in 50 mL THF followed by the addition of 2.5 mL ethyl 3-isocyanato ethylacetate. Stirring the reaction mixture under reflux for 16h resulted in the formation of a white powder that was filtered and washed with chloroform (4.8 gram). This compound was subsequently dissolved in a mixture of ethanol (50 mL) and 1 N aqueous sodium hydroxide (40 mL) and stirred for 2 h at room temperature. Addition of a saturated solution of $KHSO_4$ in water to the ice-cooled

reaction mixture until the pH=3, resulted in the formation of a white precipitate that was subsequently filtrated and washed with water. After drying in vacuo 4.4 gram of the carboxylic acid functional ureidopyrimidone was isolated.

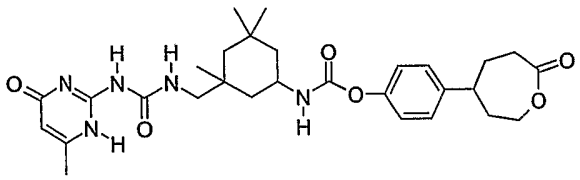
A mixture of the carboxylic acid functional ureidopyrimidone (2.0 gram), mercuric acetate (30 mg), vinylacetate (4.0 gram), and concentrated sulfuric acid (15 uL) was stirred for 2 days at 60 °C. The reaction mixture was subsequently precipitated in diethylether. After filtration and drying in vacuo, 4H vinylacetate was obtained as a white powder (2.9 gram).

*Example 12: monomer 7, a 4H hydrogen bonding unit containing styrene monomer*



Isocyanate I (5.6 g) was added to 4-aminostyrene (obtained from Aldrich 1.9 g) dissolved in 50 mL of chloroform and subsequently heated to 70 °C. The mixture was stirred under an argon atmosphere for 12h. The product was obtained by separation of the yellowish precipitate from the reaction mixture by filtration, followed by washing with chloroform. $^1$H NMR (400 MHz, $CDCl_3$/DMSO-d6): δ 7.8 (1H), 7.2 (4H), 6.6 (1H), 5.8 (1H), 5.5 (1H), 5.1 (1H), 3.4-3.2 (4H), 2.1 (3H), 1.7-1.2 (8H). FT-IR (neat): ν 3278, 2935, 1699, 1665, 1652, 1582, 1525.

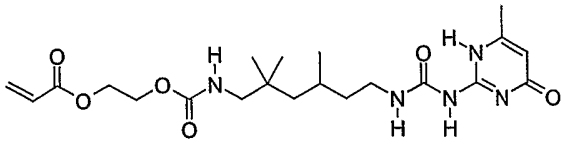
*Example 13: monomer **8**, a 4H hydrogen bonding unit containing ε-lacton monomer*



A solution of 4-(4-hydroxyphenyl)-cyclohexanone (obtained from Fluka, 8.2 g) dissolved in 100 mL of 2-butanone was added drop wise to a stirred solution of 3-chloroperoxybenzoic acid (9.3 g) in 40 mL 2-butanone. After 5h the reaction mixture was concentrated in vacuo to 30% of its original volume followed by the addition of 50 mL diethylether. The resulting white precipitate was collected by filtration and dried in vacuo. The resulting white powder was redissolved in 150 mL chloroform to which

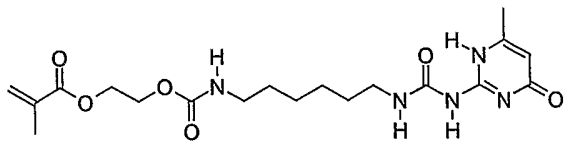
isocyanate II was added (11.8 g) and 4 drops dibutyltinlaureate. The mixture was stirred at reflux under an argon atmosphere for 16h. The product was obtained by precipitation in diethylether. $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 12.0 (1H), 10.1 (1H), 7.3-7.0 (4H), 5.9 (1H), 5.4-5.0 (1H), 4.4 (2H), 4.1-3.8 (2H), 3.2-2.6 (4H) 2.2-0.9 (22H). IR (neat): ν 3211, 2955, 1724, 1699, 1660, 1575, 1505, 1247, 1211.

*Example 14: monomer **9**, a 4H hydrogen bonding unit containing acrylate monomer*



Isocyanate IV (11 g) was dissolved in chloroform (150 mL), and thereafter hydroxy ethyl acrylate (HEA, 4.1 mL) and 4 drops of dibutyl tin dilaurate (DBTDL) were added. The mixture was stirred at an oil bath temperature of 60 °C for 9 hours, and was then cooled and precipitated in pentane, followed by a washing step with diethylether. The white powder was collected by filtration, and was washed with diethylether. Drying in vacuo gave a white solid product. $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 11.8 (1H), 10.1 (1H), 6.5 (1H), 6.2 (1H), 5.9 (2H), 5.4 and 5.1 (1H), 4.4 (4H), 3.3-2.9 (4H), 2.1 (3H), 1.8-0.9 (14H).

*Example 15: monomer **10**, a 4H hydrogen bonding unit containing methacrylate monomer*



The isocyanate (79 g) was suspended in chloroform (1.5 L), and thereafter hydroxy ethyl methacrylate (HEMA, 64 mL) and 15 drops of dibutyl tin dilaurate (DBTDL) were added. The mixture was stirred at an oil bath temperature of 90 °C for 4 hours, and was then cooled and filtered. The filtrate was concentrated and dropped into an excess of diethylether. The white precipitate was collected by filtration, and was washed with diethylether. Drying in vacuo gave a white solid product (90 g). $^1$H NMR (400 MHz, $CDCl_3$): δ 13.1 (1H), 11.8 (1H), 10.1 (1H), 6.1 (1H), 5.8 (1H), 5.6 (1H), 5.0

(1H), 4.3 (4H), 3.3-3.2 (4H), 2.1 (3H), 1.9 (3H), 1.7-1.2 (8H). FT-IR (neat): ν 3301, 2932, 1720, 1699, 1685, 1665, 1582, 1525, 1258.

**Synthesis of co-polymers**

Examples of co-polymers containing 4H hydrogen bonding units were obtained via several different polymerization techniques that are known in the art. Results can be found in Table 1, general procedures are given below:

***Atom transfer radical polymerization (ATRP) procedure***

*Preparation of poly-HEMA polymers (polymers A-E).*

A 25 mL round bottom flask containing CuBr (ca. 1 equiv. to initiator; typically 0.06 to 0.31 g), 2,2'-bipyridine (ca. 2 equiv. to initiator) and the appropriate amount of 4H hydrogen bonding unit containing monomer was degassed (de-oxygenated) by vacuum followed by argon backfill, and repeating this cycle twice. HEMA, DMSO (in equal volumes, typically both 2 to 5 mL) and optionally PEG-MA (average Mn = 360 Dalton; for polymers B and C) were degassed (de-oxygenated) by bubbling through argon for at least 45 minutes, and were then added to the 25 mL flask by use of a syringe. The reaction mixture was stirred until all components had dissolved (sometimes after short warming) to produce a homogeneous dark brown solution. The reaction flask was placed in a water bath that was maintained at room temperature, and finally, the ATRP-initiator (benzyl-2-bromo-2-methyl-propionate) was added using a syringe. The molar ratio of ATRP initiator to HEMA was about 1:40 (for polymers A, C, D and E) and about 1:20 for polymer B. Polymerization occurred immediately, leading to an increase in viscosity of the reaction mixture. After ca. half an hour, the polymer was isolated by precipitation into an EDTA (25 g/L) solution in water (polymers B-E), or in chloroform (polymer A). The polymer was washed and dried.

*Preparation of PMMA polymers (polymers F-G).*

A flask containing $NiBr_2(PPh_3)_2$ (ca. 0.35 g) and, optionally, the 4H hydrogen bonding unit containing monomer **3** was degassed (de-oxygenated) by vacuum followed by argon backfill, and repeating this cycle twice. MMA and toluene (in equal volumes; both 5 mL) were degassed (de-oxygenated) by bubbling through argon for at least 45 minutes, and were then added to the flask by use of a syringe. Finally, the ATRP-

initiator (benzyl-2-bromo-2-methyl-propionate, ca. 185 mg) was added using a syringe The flask was placed in an oil bath of 70 °C and the polymerization was allowed to run for about 20 hours. The solution was filtered over alumina and flushed with chloroform/methanol, the filtrate was concentrated and dropped into hexane. The precipitate was dried.

***Free radical polymerization (FR) procedures (polymers H-L)***

A solution containing HEMA (5 mL), the appropriate 4H hydrogen bonding unit containing monomer, AIBN (12 mg) and transfer agent mercapto ethanol (75 microliter; 60 microliter for polymer I) in DMF (15 mL), was degassed by purging with argon for 1 hr prior to polymerization. Polymerization was conducted at 80 °C for about 3 to 4 hours, after which the mixture was cooled down to room temperature and the polymer was recovered by precipitation into a non-solvent (THF/hexane 3/1 was used for polymers H and I; water was used for polymers J-L), filtration and drying. For polymer H, different conditions were used: 4.7 mL HEMA, 30 mL DMF, monomer **3**, 20 microliter mercapto ethanol and 22 mg AIBN were stirred at 60 °C for two days; the AIBN was added in two equal portions at the beginning and after 1 day of polymerization.

***Ring-opening polymerization (ROP) procedure (polymer M)***

Freshly distilled and dried ε-caprolacton, benzylalcohol (initiator) and pyridine (2 equiv. to initiator) were added to a Schlenck bottle in a nitrogen atmosphere that contained tin(II)trifluoromethanesulfonate (catalyst 0.5 equiv. to initiator) and the desired amount of monomer **8**. The Schlenck bottle was placed in an oil bath and heated to 65 °C for 16 hours. The viscous reaction mixture was diluted with an equal volume of THF and subsequently precipitated in methanol, filtered and dried in vacuo.

***Emulsion polymerization (EP) procedure (polymers N and O)***

Butyl acrylate (5 mL), water (11 mL), optionally monomer **9** (0.67 g), sodium dodecyl sulphate (0.1 g), charge transfer agent dodecyl mercaptane (0.3 mL), initiator sodium persulphate (25 mg for polymer N and 50 mg for polymer O) and sodium bicarbonate (30 mg for polymer N and 25 mg for polymer O) were mixed at 20 °C and purged with argon for 45 minutes. Subsequently, the reaction temperature was raised to 50 °C and

the mixture was extensively stirred for 4 hours. The polymer product was isolated after coagulation of the emulsion by addition of methanol.

Table 1

| Polymer | Monomer A | Monomer B | 4H-bridge monomer | Monomer molar Ratio in Feed A : (B) : 4H-mon | method | Mn (kDa) from NMR | Mn / D (kDa/-) from SEC | # of 4H-bridge monomers per chain |
|---|---|---|---|---|---|---|---|---|
| A | HEMA | - | #10 | 19.2 : 1 | ATRP | 10 | - | 1.7 |
| B | HEMA | PEG-MA | #3 | 85 : 6.5 : 8.5 | ATRP | 5.2 | 18 / 1.8 | 1.8 |
| C | HEMA | PEG-MA | #3 | 92 : 3.8 : 4.2 | ATRP | 10 | 27 / 1.6 | 2.5 |
| D | HEMA | - | #3 | 10 : 1 | ATRP | 10 | - | 3.8 |
| E | HEMA | - | #4 | 21.2 : 1 | ATRP | 6.5 | - | 1.7 |
| F | MMA | - | - | - | ATRP | - | 7.6 / 1.1 | 0 |
| G | MMA | - | #3 | 12.9 : 1 | ATRP | - | 9.4 / 1.4 | 3.7 |
| H | HEMA | - | #3 | 19.4 : 1 | FR | - | - | - |
| I | HEMA | - | #3 | 37.5 : 1 | FR | - | 24 / 1.4 | - |
| J | HEMA | - | #10 | 9.6 : 1 | FR | - | - | - |
| K | HEMA | - | #2 | 9.2 : 1 | FR | - | - | - |
| L | HEMA | - | #5 | 25.4 : 1 | FR | - | - | - |
| M | ε-CL | - | #8 | 17 : 1 | ROP | 5.1 | - | 2.8 |
| N | BA | - | #9 | 23.4 : 1 | EP | - | 15.9* | - |
| O | BA | - | - | - | EP | - | 34.8* | 0 |

- = not determined; * $M_{top}$ (kD)

***Characterization***

Molecular weights ($M_n$) of polymers A-E, and M were determined with $^1$H NMR by considering the integral of the benzylic end group versus the integral of the repeating unit. The molecular weights (Mn) and dispersities (D) of polymers B, C and I were determined with SEC (0.01 M LiBr in DMF) against polystyrene standards (a comparison with the NMR data for polymers B and C shows that the Mn and D values from the SEC-measurements are overrated). The molecular weights (Mn or Mtop) and dispersities (D) of polymers F, G, N and O were determined with SEC (THF) against polystyrene standards.

Additionally, $^1$H NMR in deuterated chloroform or DMSO-$d_6$ has been used to calculate the average number of 4H hydrogen bonding units per polymer chain by considering the integral of the benzylic signals of the polymer end group and the integral of the alkylidene signal of the 4H hydrogen bonding unit in case of polymers A-G and M. Polymers H-L and N contain incorporated 4H hydrogen bonding units, as evidenced by $^1$H NMR data.

**Polymer properties**

The effect of incorporation of 4H hydrogen bonding units in the polymer chain is clearly demonstrated in the solution (kinematic) viscosity of PMMA-samples at 20 °C, see Table 2. As can be seen, incorporation of 4H hydrogen bonding units according to this invention has a pronounced and unique thickening effect.

Table 2

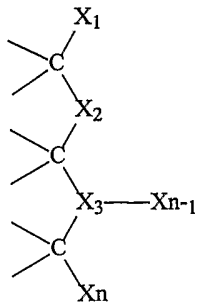
| Concentration in chloroform (g/L) | Kinematic viscosity polymer F ($mm^2/s$) | Concentration in chloroform (g/L) | Kinematic viscosity polymer G ($mm^2/s$) |
|---|---|---|---|
| 44 | 0.61 | 22 | 0.53 |
| 81 | 0.74 | 30 | 0.58 |
| 115 | 0.97 | 44 | 0.76 |
| 163 | 1.37 | 68 | 1.10 |
| 226 | 2.24 | 92 | 1.85 |
| 280 | 3.41 | 128 | 5.49 |

polymer F and G have a comparable molecular weight, see table 1.

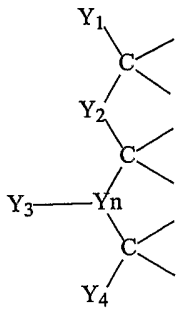
Incorporation of 4H hydrogen bonding units in polymers according to this invention also gives enhancement in material properties, as most clearly reflected in the difference in properties of polymers N and O. While poly(butylacrylate) O is a sticky viscous liquid, poly(butylacrylate) N with incorporated 4H hydrogen bonding units is an elastic material even despite the fact that polymer N has a lower molecular weight than polymer O.

## CLAIMS

1. A monomer comprising (a) a monomeric unit having a group that can be polymerized (i.e. a monomeric unit having a polymerizable group), a linking moiety (b) and a structural element (c) capable of forming at least four hydrogen bridges, wherein the monomer has the general structure (a) - (b) - (c).
2. The monomer according to claim 1, wherein the structural element (c) has the general form (1) or (2):



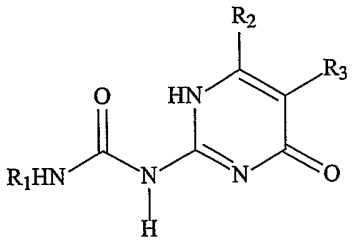
(1')



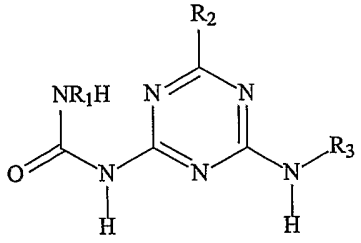
(2')

wherein the C-$X_i$ ($i$ = 1 - 4) and the C-$Y_i$ ($i$ = 1 - 4) linkages each represent a single or double bond and $X_i$ represent donors or acceptors that form hydrogen bridges with the H-bridge forming monomeric unit containing a corresponding general form (2) linked to them with $X_i$ representing a donor and $Y_i$ an acceptor or vice versa.

3. The monomer according to claim 2, wherein $X_1$ and $X_2$ are donors and $X_3$ and $X_4$ are acceptors.
4. The monomer according to claim 2, wherein the donors and acceptors are O, S, and N atoms.
5. The monomer according to claim 2, wherein the structural element (c) has the general formula (3) or (4), or tautomers thereof:




(3)




(4)

wherein the structural element (c) is bonded to the linking moiety (b) at $R_1$, $R_2$ or $R_3$ (so that $R_1$, $R_2$ or $R_3$ represent a direct bond) with the other R groups representing a random side chain or are hydrogen atoms.

6. A process for the preparation of a monomer as defined in claim 1, wherein a monomeric unit having a polymerizable group is reacted in a first step with a compound having at least two functional groups and wherein the product obtained in the first step is reacted with a nitrogen containing compound.

7. A process for the preparation of a monomer as defined in claim 1, wherein a nitrogen containing compound is reacted in a first step with a compound having at least two functional groups and wherein the product obtained in the first step is reacted with a monomeric unit having a polymerizable group.

8. A process for the preparation of a monomer as defined in claim 1, wherein the nitrogen containing compound is reacted directly with the monomeric unit having a polymerizable group wherein the monomeric unit is able to form a urea linkage between both reactants.

9. A copolymer comprising the monomer as defined in claim 1 and at least one comonomer.

10. The copolymer according to claim 9, wherein the comonomer is selected from the group of: acrylic acid; $C_1$-$C_{30}$ branched or linear alkyl esters of acrylic acid; methacrylic acid; $C_1$-$C_{30}$ branched or linear alkyl esters of methacrylic acid; acrylamides or methacrylamides wherein the amide group may be substituted with one or two $C_1$-$C_{30}$ branched or linear alkyl groups; vinyl esters, preferably vinyl acetates; other compounds having a vinyl group wherein said compounds are preferably selected from pyrrolidones, imidazoles, pyridines, caprolactams, piperidones, benzene and derivatives thereof; $C_4$-$C_{20}$ alkadienes; lactones; lactams;

and saturated or unsaturated heterocyclic compounds containing one to five oxygen atoms.

11. The copolymer according to claim 9, wherein the copolymer is a linear, branched, star, hyperbranched, dendritic or comb-like copolymer

12. The copolymer according to claim 9, wherein the copolymer has a random, regular, tapered or block structure.

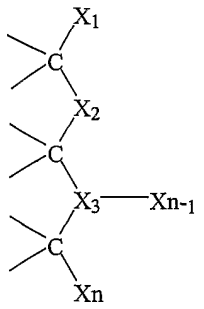
13. A process for the preparation of a copolymer, wherein a monomer as defined in claim 1 is polymerized with at least one comonomer.

14. The process according to claim 13, wherein the process is conducted in bulk, dispersion, solution, emulsion, suspension or inverse phase emulsion.

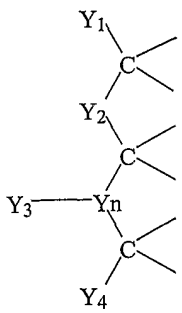
# AMENDED CLAIMS

**[Received by the International Bureau on 15 January 2004 (15.01.04): original claims 1-14 replaced by amended claims 1-14; (3 pages)]**

1. A monomer comprising (a) a monomeric unit having a group that can be polymerized (i.e. a monomeric unit having a polymerizable group), a linking moiety (b) and a structural element (c) capable of forming at least four hydrogen bridges, wherein the monomer has the general structure (a) - (b) - (c) and wherein the linking moiety (b) is derived from a compound that must have at least two functional; groups, and wherein the structural element (c) has the general form (1) or (2):




(1')




(2')

wherein the C-$X_i$ ($i$ = 1 - 4) and the C-$Y_i$ ($i$ = 1 - 4) linkages each represent a single or double bond, n is 4 or more and $X_i$ (or $X_1$ ... $X_n$) represent donors or acceptors that form hydrogen bridges with the H-bridge forming monomeric unit containing a corresponding general form (2') linked to them with $X_i$ representing a donor and $Y_i$ an acceptor or vice versa.

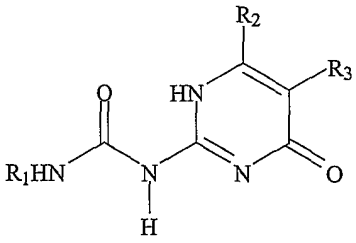
2. The monomer according to claim 1, wherein the functional groups are end groups.

3. The monomer according to claim 1 or claim 2, wherein the functional end groups are selected from hydroxy, carboxylate, carboxylic ester, ester halide, isocyanate, thioisocyanate, primary amine, secondary amine and halogen.

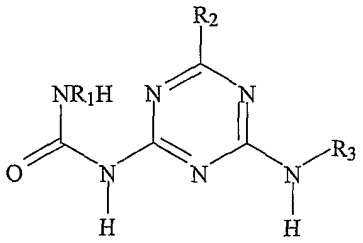
4. The monomer according to any one of claims 1 - 3, wherein $X_1$ and $X_2$ are donors and $X_3$ and $X_4$ are acceptors.

5. The monomer according to any one of claims 1 - 4, wherein the donors and acceptors are O, S, and N atoms.

6. The monomer according to any one of claims 1 - 5, wherein the structural element (c) has the general formula (3) or (4), or tautomers thereof:



(3)



(4)

wherein the structural element (c) is bonded to the linking moiety (b) at $R_1$, $R_2$ or $R_3$ (so that $R_1$, $R_2$ or $R_3$ represent a direct bond) with the other R groups representing a random side chain or are hydrogen atoms.

7. A process for the preparation of a monomer as defined in any one of claims 1 - 6, wherein a monomeric unit having a polymerizable group is reacted in a first step with a compound having at least two functional groups and wherein the product obtained in the first step is reacted with a nitrogen containing compound.

8. A process for the preparation of a monomer as defined in any one of claims 1 - 6, wherein a nitrogen containing compound is reacted in a first step with a compound having at least two functional groups and wherein the product obtained in the first step is reacted with a monomeric unit having a polymerizable group.

9. A copolymer comprising the monomer as defined in any one of claims 1 - 6 and at least one comonomer.

10. The copolymer according to claim 9, wherein the comonomer is selected from the group of: acrylic acid; $C_1$-$C_{30}$ branched or linear alkyl esters of acrylic acid; methacrylic acid; $C_1$-$C_{30}$ branched or linear alkyl esters of methacrylic acid; acrylamides or methacrylamides wherein the amide group may be substituted with one or two $C_1$-$C_{30}$ branched or linear alkyl groups; vinyl esters, preferably vinyl acetates; other compounds having a vinyl group wherein said compounds are preferably selected from pyrrolidones, imidazoles, pyridines, caprolactams, piperidones, benzene and derivatives thereof; $C_4$-$C_{20}$ alkadienes; lactones; lactams; and saturated or unsaturated heterocyclic compounds containing one to five oxygen atoms.

11. The copolymer according to claim 9 or claim 10, wherein the copolymer is a linear, branched, star, hyperbranched, dendritic or comb-like copolymer
12. The copolymer according to any one of claims 9 - 11, wherein the copolymer has a random, regular, tapered or block structure.
13. A process for the preparation of a copolymer, wherein a monomer as defined in any one of claims 1 - 6 is polymerized with at least one comonomer.
14. The process according to claim 13, wherein the process is conducted in bulk, dispersion, solution, emulsion, suspension or inverse phase emulsion.

# INTERNATIONAL SEARCH REPORT

Int al Application No
PCT/NL 03/00586

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D239/46 C08F236/20 C07D405/12

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 7 C07D C08F

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)
EPO-Internal, PAJ, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X,P | YAMAUCHI, K; LIZOTTE, J.R., LONG, T.E.: "Thermoreversible poly(alkyl acrylates) consisting of self-complementary multiple hydrogen bonding" MACROMOLECULES, vol. 36, no. 4, 2003, pages 1083-1088, XP002260387 SCMHB methacrylate (I); Scheme 2 --- -/-- | 1,5,8-14 |

[X] Further documents are listed in the continuation of box C.

[X] 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.

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 5 November 2003 | 17/11/2003 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31–70) 340–2040, Tx. 31 651 epo nl,<br>Fax: (+31–70) 340–3016 | Johnson, C |

# INTERNATIONAL SEARCH REPORT

Inte ll Application No
PCT/NL 03/00586

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | RIETH, L.R., EATON, R.F., COATES, G.W.: "Polymerization of ureidopyrimidinone-functionalized olefines by using late-transition metal Ziegler-Natta catalysts: synthesis of thermoplastic elastomeric polyolefins" ANGEW. CHEM. INT. ED. , vol. 40, no. 11, 2001, pages 2153-2156, XP002260388 Weinheim cited in the application the whole document | 1,5,9-14 |
| X | EP 0 624 605 A (CYTEC TECH CORP) 17 November 1994 (1994-11-17) page 5, line 24 - line 54; examples 1,2 | 1,5,8-14 |
| X | US 6 320 018 B1 (SIJBESMA RINTJE P ET AL) 20 November 2001 (2001-11-20) cited in the application column 1, line 65 -column 4, line 30; examples X,XIII | 1,5,8 |
| X | HERWEH, J.E. & WHITMORE, W.Y.: "Synthesis and Characterization of 2-Ureylene-4,6-diamino-s-triazines" J. CHEM. ENG. DATA, vol. 15, no. 4, 1970, pages 593-595, XP002260389 Compd IIb | 1,5,8 |
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| X | EL-GHAYOURY, A. ET AL.: "Supramolecular hydrogen-bonded oligo(p-phenylene vinylene) polymers" ANGEW. CHEM. INT. ED., vol. 40, no. 19, 2001, page 3660-3663 XP002260390 MOPVUP, BOPVUP | 1,5 |

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# INTERNATIONAL SEARCH REPORT

Int al Application No
PCT/NL 03/00586

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EL-GHAYOURY, A. ET AL.: "Quadruple hydrogen bonded oligo(p-phenylene vinylene) dimers" CHEM. COMMUN., 2000, pages 1969-1970, XP002260391 OPV3UP, OPV4UP1, OPV4UP2 | 1,5 |
| X | US 2 694 687 A (DE BENNEVILLE PETER L ET AL) 16 November 1954 (1954-11-16) claims 1-12 | 1,9-14 |
| X | US 2 744 943 A (DE BENNEVILLE PETER L ET AL) 8 May 1956 (1956-05-08) claims 1-15 | 1,9-14 |
| X | FR 1 350 973 A (GEIGY AG J R) 31 January 1964 (1964-01-31) claim 1 | 1,9-14 |
| X | US 2 461 943 A (AMERICAN CYANAMID COMPANY) claims 1-7; examples 1-4,7-10 | 1 |

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1(part), 2-4, 5(part),9-14(part)

In claim 2 the definition of n, the X3-Xn-1 bond and the Y3-Yn bond is missing. This claim therefore lacks clarity within the meaning of Article 6 PCT. The description does not clarify the meanings of these variables. Claim 2 and its dependent claims 3 and 4, which do not contain any further information clarifying the above-mentioned variables have therefore not been searched.

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty of claims 1, 5 and 9-14. So many documents were retrieved that it is impossible to determine which parts of the claim(s) may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). The documents cited in the search report represent a mere selection of the novelty-destroying documents found.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

# INTERNATIONAL SEARCH REPORT

ational application No.
PCT/NL 03/00586

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1(part), 2-4, 5(part),9-14(part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Int ıal Application No
PCT/NL 03/00586

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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