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(54) Titre : POLYMER PERMETTANT LA FORMATION D'UN POLYMER SUPRAMOLECULAIRE
(54) Title: SUPRAMOLECULAR POLYMER FORMING POLYMER

(57) **Abrégé/Abstract:**

The invention provides a polymer having the following general formula (I): where PU is a polymer chain comprising at least one polyurethane chain; and n ranges from 0 to 8; X, Y and Z, identical or different are H-bonding sites. The invention also provides a supramolecular polymer comprising units that form H-bonds with one another, wherein at least one of these units is a polymer according to the invention. The supramolecular polymer is useful as an hot melt adhesive, in rotational or slush molding, in injection molding and in the manufacture of TPU foams. The invention also provides a process for the preparation of the polymer.



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(54) Title: SUPRAMOLECULAR POLYMER FORMING POLYMER

(57) **Abstract:** The invention provides a polymer having the following general formula (I): where PU is a polymer chain comprising at least one polyurethane chain; and n ranges from 0 to 8; X, Y and Z, identical or different are H-bonding sites. The invention also provides a supramolecular polymer comprising units that form H-bonds with one another, wherein at least one of these units is a polymer according to the invention. The supramolecular polymer is useful as an hot melt adhesive, in rotational or slush molding, in injection molding and in the manufacture of TPU foams. The invention also provides a process for the preparation of the polymer.



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SUPRAMOLECULAR POLYMER FORMING POLYMER

This invention relates to a polymer which is able to form a supramolecular polymer, to the preparation of such a polymer and to the uses of the formed supramolecular polymer.

It is known for several years that supramolecular polymers are polymers in which the monomers are at least in part bond to one another via H-bridges.

When the monomer units have a low molecular weight, they form at low temperature a rigid dimensionally stable polymer. At higher temperatures however, since the H-bridges are much weaker, essentially only monomeric units are present and can be easily handled.

International Patent Application No. WO 98/14504 discloses a 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. As H-bridge-forming monomeric units, substituted ureido-pyrimidones and ureido-pyrimidines were used. In examples XII and XIII of that International Patent Application is described the end-capping of polydimethyltrisiloxanes with 4-benzyloxy-6-(3-butenyl)-2-butylureidopyrimidine and 6-(3-butenyl)-2-butylureido—4-pyrimidone, respectively.

In "Reversible Polymers Formed from Self-Complementary Monomers Using Quadruple Hydrogen Bonding", by R.P. Sijbesma, H.B. Beijer, L. Brunsveld, B.J.B. Folmer, J.H.K. Ky Hirschberg, R.F.M. Lange, J.K.L. Lowe, E.W. Meijer, published in Science, Vol. 278, 28 November 1997, is disclosed in Fig. 2 the reaction of 6-tridecylisocytosine with hexanediisocyanate to give a bifunctional compound (2a) which forms reversible polymers. In Fig. 6 of that reference is also disclosed the functionalization of a trifunctional copolymer of propylene oxide and ethylene oxide with a diisocyanate, followed by a reaction with methylisocytosine to give a compound (7) which has the ability to form reversible polymer networks. These compounds (2a) and (7) are supposed to allow the formation of polymer networks that can be used in hot melts and coatings. However, as indicated in the reference, compound (2a) has a tendency to crystallise and compound (7) exhibits poor mechanical properties.

In "New Polymers Based on the Quadruple Hydrogen Bonding Motif", by Brigitte J.B. Folmer, pages 91-108, PhD Thesis, Technische Universiteit Eindhoven, 2000, is disclosed (see in particular page 96) the end-capping of hydroxy terminated polymers with a reactive synthon obtained by the reaction of methylisocytosine with 1,6-
 5 hexanediisocyanate. The hydroxy terminated polymers are a hydrogenated polybutadiene, a polyether, a polycarbonate and a polyester.

However, the mechanical strength of these materials is relatively low, and softening of the materials typically occur at relatively low temperatures which can therefore limit
 10 their practical utility.

An object of this invention is therefore to provide a polymer which is able to form a supramolecular polymer. This polymer has the following general formula :



where

20 PU is a polymer chain comprising at least one polyurethane chain; and
 n ranges from 0 to 8;
 X, Y and Z, identical or different are H-bonding sites.

Another object of this invention is a supramolecular polymer formed at least from the
 25 polymer of the invention. Such a supramolecular polymer comprises units that form H-bridges with one another, wherein at least one of these units is the above polymer.

Such a supramolecular polymer combines good mechanical properties such as elongation, yield stress and low melt viscosities.

30

A further object of this invention is to provide a process for the preparation of the above polymer. This process comprises the step of reacting a polymer comprising at least one polyurethane chain and at least two free -NCO groups with at least one compound A having at least one group able to react a -NCO group and at least one H-bonding site.

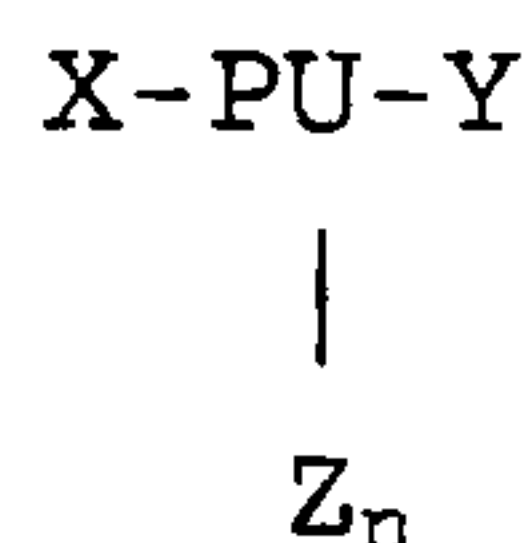
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Other objects, features and advantages will become more apparent after referring to the following specification.

The polymer of the invention has the following general formula :

5



10 where

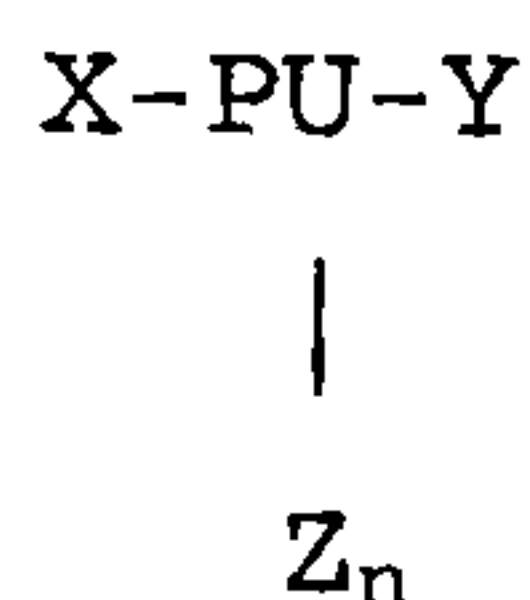
PU is a polymer chain comprising at least one polyurethane chain;

n ranges from 0 to 8; and

15 X, Y and Z are identical or different and are H-bonding sites.

Another object of this invention provides a process for the preparation of a polymer having the following general formula :

20



wherein:

25 PU is a polymer chain comprising at least one polyurethane chain; and

n ranges from 0 to 8;

X, Y and Z, identical or different, are H-bonding sites; comprising reacting a) a polyisocyanate with a functionality

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3a

of 2, the polyisocyanate being diphenylmethane diisocyanate,
b) a polyol having a MW from 750 to 6000 and a functionality
from 1.9 to 2.5, c) a polyol having a MW from 62 to 750 with
a functionality of 1.9 to 2.1, and d) an amine compound of
5 formula $H_2N-C(R_3)=N-R_4$, wherein R_3 and R_4 are each
independently a C1-C6 alkyl or a C3-C6 cycloalkyl, or
together can form a ring having one or two cycle(s), all
being optionally interrupted by one or more heteroatom(s),
wherein the heteroatom is N, O or S, with a MW less
10 than 400;

wherein the amount of isocyanate a), polyol b), polyol c)
and amine d) is 10-50, 35-90, 1-30 and 0.5-20 by weight
respectively per 100 parts by weight of isocyanate a),
polyol b) polyol c) and amine d), wherein the reaction is
15 conducted at an isocyanate index of 90 to 200.

Another object of this invention provides a supramolecular
polymer comprising units that form H-bonds with one another,
wherein at least one of these units is a polymer obtained by
the process as defined herein.

20 Another object of this invention provides the use of a
supramolecular polymer as defined herein, as an hot melt
adhesive; in rotational or slush molding; in injection
molding; or in the manufacture of TPU foams.

Polyurethane chain PU

25 According to the invention, the polymer chain PU comprises
at least one polyurethane chain.

According to one embodiment, the PU is thermoplastic and/or
elastomeric.

According to another embodiment, the polyurethane chain
30 preferably comprises at least one soft block and at least

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3b

two hard blocks. The soft and hard blocks are according to the common general knowledge in the art.

The polyurethane chain may have a molecular weight (MWn) ranging between large limits. The molecular weight is
5 calculated according to the Dryadd Pro model (1998, Oxford Materials Ltd, UK). It generally has a low average molecular weight, i.e., an average molecular weight of less than 50000. Preferably, the average molecular weight is in the range of 2000 to 50000. More preferably, the average
10 molecular weight is between 5000 and 40000.

This PU chain is obtained by classical methods known in the art (see for example Polyurethanes Handbook 2nd edition, G. Oertel, 1994). The chains are notably obtained

by the reaction of an isocyanate, an isocyanate-reactive compound (a polyol) and a chain extender.

For example, the suitable organic polyisocyanates for use in the process of the present invention include any of those known in the art for the preparation of polyurethanes., and in particular the aromatic polyisocyanates such as diphenylmethane diisocyanate in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, although these are not preferred, toluene diisocyanate in the form of its 2,4- and 2,6-isomers and mixtures thereof, 1,5-naphthalene diisocyanate and 1,4-diisocyanatobenzene. Other organic polyisocyanates which may be mentioned include the aliphatic diisocyanates such as isophorone diisocyanate, 1,6-diisocyanatohexane and 4,4'-diisocyanatodicyclo-hexylmethane. Preferred are TDI or MDI, IPDI, HMDI and other aliphatic isocyanates. Most preferred is MDI, especially 4,4'-MDI. The functionality is preferably 2. Mixtures may be used.

Suitable isocyanate-reactive compounds to be used in the process of the present invention include any of those known in the art for the preparation of polyurethanes. Of particular importance are polyols and polyol mixtures having average hydroxyl numbers of from 20 to 300, especially from 25 to 150 mg KOH/g, and hydroxyl functionalities of from 1.5 to 3, especially from 1.8 to 2.2, and a MW generally from 750 to 6000. Suitable polyols have been fully described in the prior art and include reaction products of alkylene oxides, for example ethylene oxide and/or propylene oxide, with initiators containing from 2 to 8 active hydrogen atoms per molecule. Suitable initiators include: polyols, for example glycerol, trimethylolpropane, triethanolamine, pentaerythritol, sorbitol and sucrose; polyamines, for example ethylene diamine, tolylene diamine (TDA), diaminodiphenylmethane (DADPM) and polymethylene polyphenylene polyamines; and aminoalcohols, for example ethanolamine and diethanolamine; and mixtures of such initiators. Other suitable polymeric polyols include polyesters obtained by the condensation of appropriate proportions of glycols and higher functionality polyols with dicarboxylic or polycarboxylic acids. Still further suitable polymeric polyols include hydroxyl terminated polythioethers, polyamides, polyesteramides, polycarbonates,

polyacetals, polyolefins and polysiloxanes. The isocyanate-reactive compound is preferably a polyol which is preferably a polyether or a polyester or mixtures thereof. Mixtures may be used.

5 A chain extender is classically used; it is traditionally a low molecular weight polyol, typically a diol. The MW generally ranges from 62 to 750; the functionality generally ranges from 1.9 to 2.1. Examples of suitable diols include ethylene glycol, diethylene glycol, butanediol, triethylene glycol, tripropylene glycol, 2-hydroxyethyl-2'-hydroxypropylether, 1,2-propylene glycol, 1,3-propylene glycol, Pripol® (Uniquema,
10 Gouda, NL), dipropyl glycol, 1,2-, 1,3- and 1,4-butylene glycols, 1,5-pentane diol, bis-2-hydroxypropyl sulphide, bis-2-hydroxyalkyl carbonates, p-xylylene glycol, 4-hydroxymethyl-2,6-dimethyl phenol and 1,2-, 1,3- and 1,4-dihydroxy benzenes. PEG, PPG (e.g. 200) as well as PTHF (also known as PTMG) (e.g. 400) may also be used. Mixtures may be used.

15

Optional trifunctional chain extenders such as glycerol, trimethylolpropane and its alkoxylated derivatives may be used in combination with bifunctional chain extenders.

The quantities of the polyisocyanate compositions and the polyfunctional isocyanate-
20 reactive compositions as well as those of the chain extender to be reacted (in the absence of end-cap monomer) will depend upon the nature of the polyurethane to be produced and will be readily determined by those skilled in the art. The isocyanate index can vary within broad limits, such as between 80 and 400.

25 **H-bonding groups**

According to the invention, the polymer chain PU bears the H-bonding groups X and Y, and optionally Z, which are identical or different.

30 Preferably, X and Y, identical, are the end groups of the polymer chain PU.

Generally, the H-bonding groups X and Y (and Z) have at least two sites capable of H-donor capability and at least two sites capable of H-acceptor capability (where these two sites may not be fully reacted).

The H-donor site may be a H-donor group well known by those skilled in the art. Such an H-donor group may comprise -NH-, -OH or -SH groups.

- 5 The H-acceptor site may be a H-acceptor site well known by those skilled in the art. Such an H-acceptor site may comprise atoms like O, N or S.

According to a preferred embodiment of the invention, X and Y (and Z) includes the group -NH-CO-NH-.

10

According to a highly preferred embodiment, X and Y are obtained by the reaction of a terminal isocyanate group with a compound of formula $H_2N-R_1R_2$, where R_1 and R_2 are each independently a C1-C6 alkyl or C3-C6 cycloalkyl group, or together can form a ring having one or two cycle(s), one or both of R_1 and R_2 being optionally interrupted by one or more heteroatom(s) selected from N, O and S.

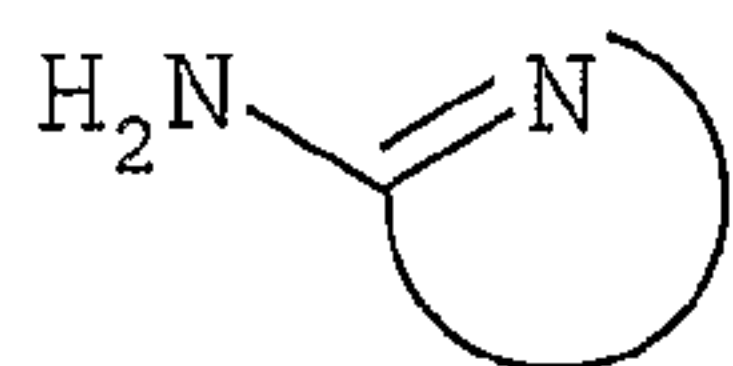
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The amine can be of formula $H_2N-C(R_3)=N-R_4$, where R_3 and R_4 are each independently a C1-C6 alkyl or C3-C6 cycloalkyl group, or together can form a ring having one or two cycle(s), one or both of R_3 and R_4 being optionally interrupted by one or more heteroatom(s) selected from N, O and S.

20

Preferably, at least one of R_1 and R_2 or R_3 and R_4 respectively is interrupted by one or more heteroatom(s).

- 25 Preferably, the amine is of formula



where the curve is a ring having one or two cycles, optionally interrupted by one or two heteroatoms selected from N, O and S.

- 30 The molecular weight is preferably below 400.

Preferably, the H-bonding site of the compound A reacting with the -NCO group is adjacent to the group which reacts with the -NCO group of the polymer.

The amine can be selected from the group consisting of 2-aminopyrimidine, isocytosine, 6-alkylisocytosine such as 6-methylisocytosine, 2-aminopyridine, 5-amino-uracil 6-tridecylisocytosine, 6-phenyl-isocytosine, 2-amino-6-(3-butenyl)-4-pyrimidone, p-di-(2-amino-6-ethyl-4-pyrimidone) benzene, 2-amino 4-pyridone, 4-pyrimidone 6-methyl-2-amino-4-pyrimidone, 6-ethyl-2-amino-4-pyrimidone, 6-phenyl-2-amino-4-pyrimidone, 6-(p-nitrophenyl)isocytosine, 6-(trifluoromethyl) isocytosine and their mixtures.

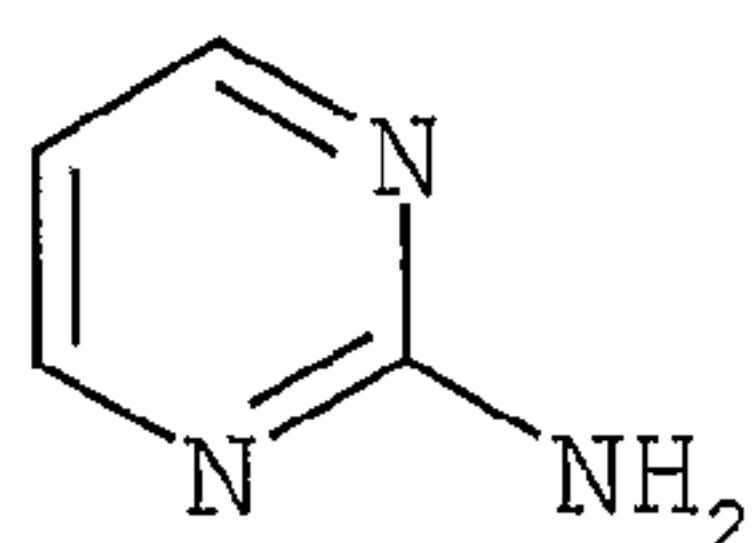
Examples of such compounds are 2-aminopyrimidine, 5-aminouracil, isocytosine and 6-alkylisocytosine such as 6-methylisocytosine.

The preferred amines are 2-aminopyrimidine and 6-alkylisocytosine such as 6-methylisocytosine.

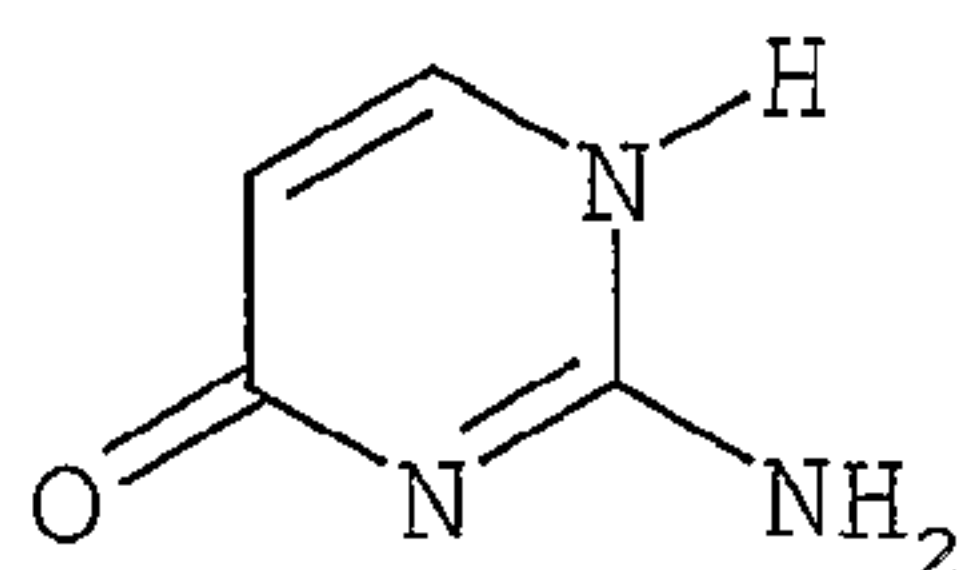
The weight percentage of the groups X and Y based on the weight of the entire polymer of the invention generally ranges from 0.05 to 20% and preferably from 0.1 to 5%.

For example, one can cite as amine compounds the following compounds:

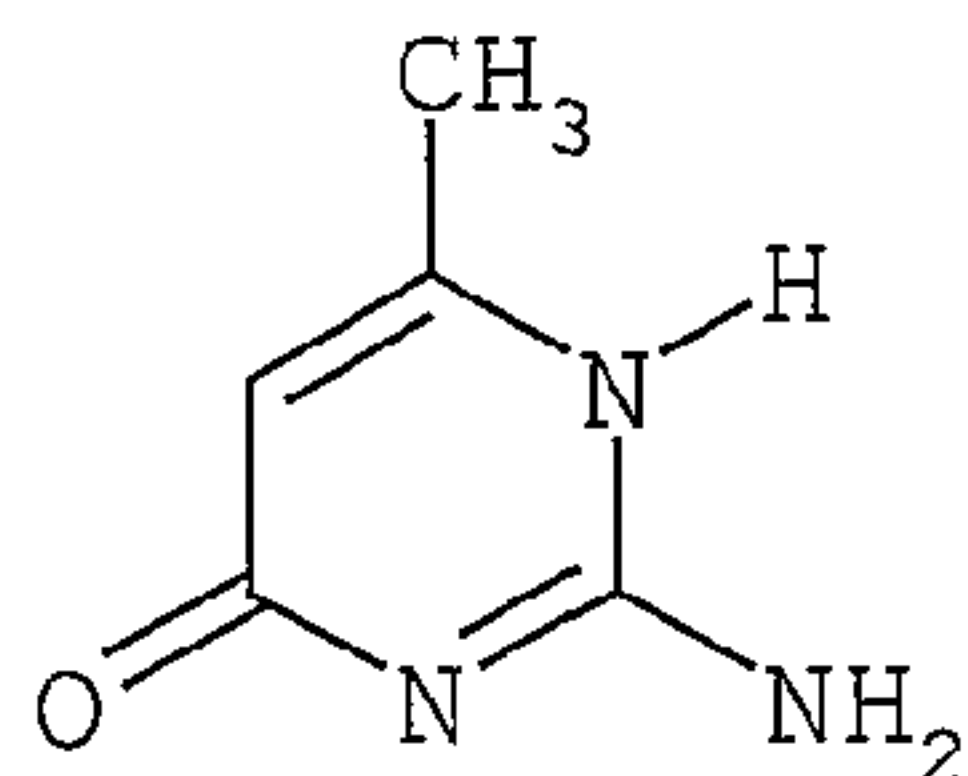
2-aminopyrimidine (AP): (formula)



isocytosine : (formula)



6-methylisocytosine (Melso) : (formula)



Process according to the invention

The polymer of the invention may be prepared according to a process comprising the
 5 step of reacting a polymer comprising at least one polyurethane chain and at least two
 free –NCO groups with at least one compound A having at least one group able to react
 a –NCO group and at least one H-bonding site.

This compound A is described above.

10

2-aminopyrimidine is one of the preferred reactants, since its melting point is quite low,
 about 125°C. This is interesting from a production viewpoint, because it allows to
 prepare the polymer of the invention at lower temperatures.

15 6-alkylisocytosine such as 6-methylisocytosine is one of the preferred reactants, because
 of the powerful effect, i.e. the resulting (supra)polymer exhibits high mechanical
 properties with low viscosities at melt.

A preferred process is one in which the polymers are obtained by reacting a
 20 polyisocyanate (1) with a functionality of 2, a polyol (2) having a MW from 750 to 6000
 and a functionality from 1.8 to 2.2, a polyol (3) having a MW from 62 to 750 with a
 functionality of 1.9 to 2.5 and an amine compound (4) of formula $H_2N-C(R_3)=N-R_4$,
 where R_3 and R_4 are each independently a C1-C6 alkyl or C3-C6 cycloalkyl group, or
 together can form a ring having one or two cycle(s), all being optionally interrupted by
 25 one or more heteroatom(s) selected from N, O and S, with a MW less than 400 wherein
 the amount of isocyanate (1), polyol (2), polyol (3) and amine (4) is 10-50, 35-90, 1-30
 and 0.5-20 by weight respectively per 100 parts by weight of isocyanate (1), polyol (2),
 polyol (3) and amine (4) wherein the reaction is conducted at an isocyanate index of 90
 to 200, preferably 95 to 150, especially 98 to 102.

The above index also applies to any general process involving the reaction of polyisocyanate compositions, polyfunctional isocyanate-reactive compositions, chain extender and end-cap monomer (or compound A).

5

The polymers can be synthesised by either a solution or a bulk reaction process. In both cases, isocyanate (1), polyol (2), polyol (3) and amine (4) can be polymerised in a one-step process in the presence of a suitable catalyst in order to achieve the desired product. Alternatively, isocyanate (1) may be prepolymerised with polyol (2) and subsequently
10 co-reacted with a blend of polyol (3) and amine (4) to obtain said product. This route of making polymers also allows producing polymers of the invention with high amounts of polyol (3). Such polymers are particularly useful in hot melt adhesive type applications. In order to accommodate this synthetic versatility without the occurrence of undesired covalent chain extension or cross-linking, dependent on the number of primary amine
15 groups of amine (4), it is essential that amine (4) contains a single primary amine group. An amine with only one primary amine group allows controlling the polymer structure and polymer molecular weight precisely.

In a preferred embodiment, the polymer is obtained by bulk polymerisation of the
20 components in the presence of mechanical shear, for example within the chambers of a Banbury.RTM.type mixer or twin-screw extruder. In the bulk polymerisation, it is preferred that the powdered amine (4) is milled to a suitably small particle size in order to facilitate rapid and efficient reaction.

25

Supramolecular polymers of the invention

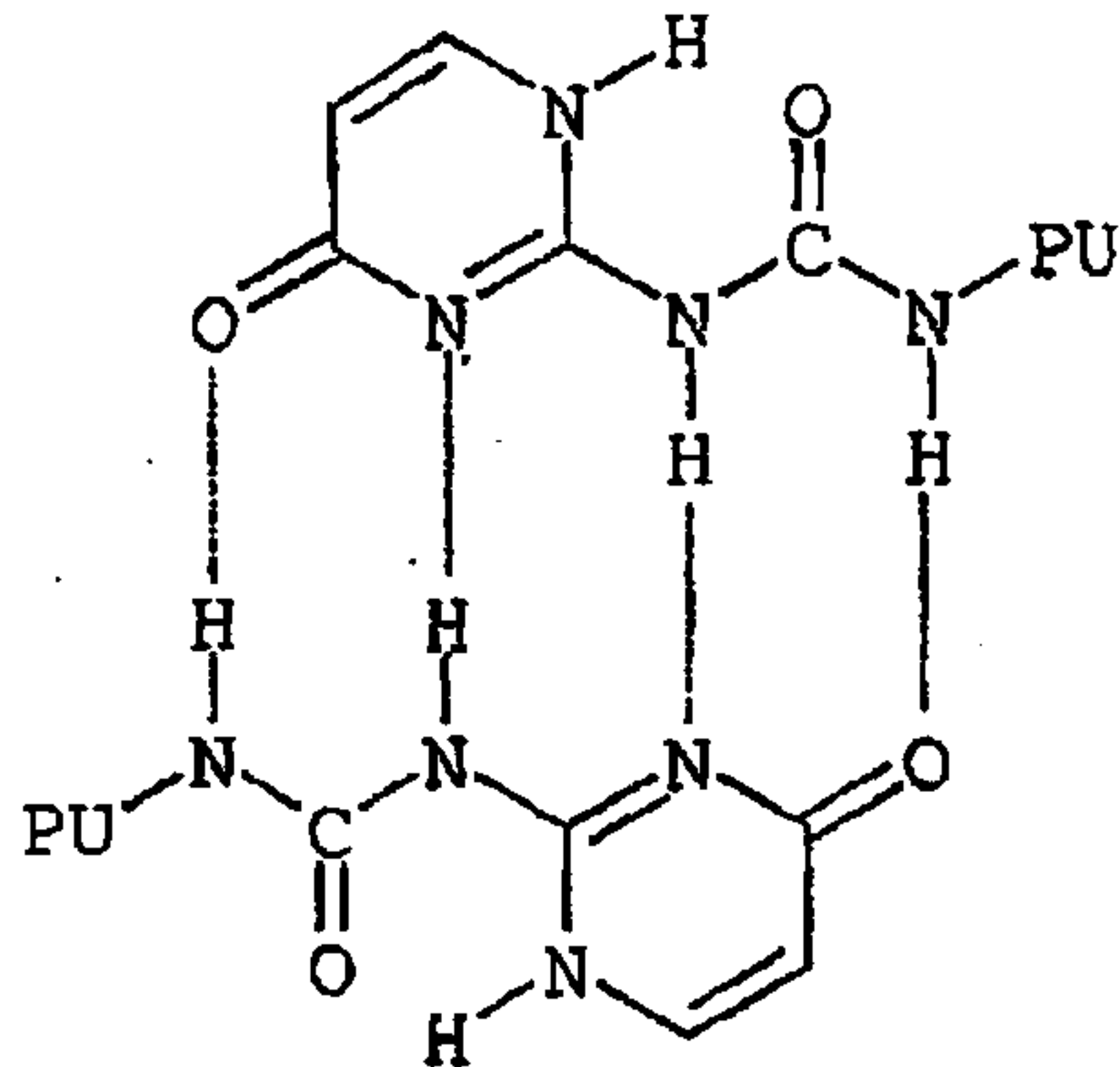
Thanks to its H-bonding groups X and Y, the polymer of the invention has the ability to allow the formation of a supramolecular polymer at room temperature.

30

This is represented below, with isocytosine as an example. The dotted lines represent the H-bonds.

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10



Therefore, an object of the invention is also a supramolecular polymer comprising units
 5 that form H-bridges with one another, and in which at least one of these units is a
 polymer according to the invention as described above.

The remaining units can be different units, for example, units as described in aforesaid
 International Patent Application No. WO 98/14504. Preferably the units are the same.

10

In the polymer of the invention, the groups X and Y generate thermoreversible linear
 chain extension through H-bonding interactions.

Thus the units have the capability to auto chain extend by chain-end interaction through
 15 H-bonding interaction.

Since the H bonds are thermoreversible, at low temperatures, the H-bond interaction is
 high and the supramolecular polymer has an apparent high molecular weight. At high
 temperatures, the H-bond interaction does not exist anymore or is low and the
 20 supramolecular polymer mainly decomposes into its monomeric units and behaves as a
 low molecular weight polymer.

In other words, when heated, the hydrogen bonds break and give a low viscosity
 material. Therefore, the supramolecular polymer has pseudo-high molecular weight
 25 properties at room temperature but low molecular weight properties at melt.

Without wishing to be bound by theory, it is believed that the temperature at which the melting transition occurs in the polymers of the current invention is controlled by the design of the hard block. This transition temperature may be equal to or higher than the temperature at which the H-bonding interactions between the chain-ends are predominantly dissociated. Typically, the dissociation temperature of the end-group H-bonding interactions is greater than 80°C and the hard block melting temperature is greater than 100°C. The ability to systematically control the melting temperature of the polymer through hard block design and the weight percentage of the hard block material in the polymer is an additional advantage of the polymers according to the present invention.

Uses of the supramolecular polymer of the invention

The supramolecular polymer of the invention can generally be used in all applications where the PUs (such as those forming the PU chain) are used.

Hot melts adhesive is one of the preferred applications. In this case, a unique feature of the supramolecular polymer of the invention is that it provides an adhesive having no unreacted NCO group (unlike reactive hot-melts that require water to fully cure). This is also an advantage in terms of safety and handling. Another unique feature of the supramolecular polymer of the invention is that it does not require solvent, unlike known solvent-borne TPU adhesives.

Another advantage provided by the supramolecular polymer of the invention is that it does not need moisture to reach ultimate mechanical properties. As such, it can be used in adhesive applications of non-moisture permeable substrates like Al-Al joints.

Another application is rotational and/or slush molding, since fluidity is very high under the conditions used, ensuring a good spread in the mold. Still another application is injection molding and the manufacture of TPU foams.

The main advantage of the supramolecular polymers is their lower viscosity at melt than the uncapped ones (which do not form supramolecular polymers). This allows easier

processing, while retaining good mechanical properties at room temperature. To evaluate their efficiency, the properties were plotted versus viscosity at melt, since an increase in melt viscosity corresponds to an increase in the molecular weight.

5 **Examples**

Example 1

Prepolymer 1 was prepared by stirring a mixture of 73pbw of a polypropyleneoxide (PPG2000) having a nominal functionality of 2 and nominal MW 2000 together with 27pbw "Suprasec® MPR" (4,4' MDI less than 2% of the 2,4' MDI isomer) at 87°C under nitrogen for three hours. After cooling, the prepolymer was stored as a masterbatch under nitrogen.

15 A pre-calculated amount of 1,4-butanediol BD (50wt% solution in dimethylacetamide) was added dropwise over a period of 20 minutes to a known amount of a stirred 50wt% dimethylacetamide solution of the prepolymer at 87°C under nitrogen and the heating/stirring were maintained for a further 3 hours. A dimethylacetamide solution of the desired end-capping compound was added to the stirred reaction mixture at 87°C and
20 the reaction conditions were maintained for a further 3 hours. After cooling, the polymer was isolated by casting at 50°C in a vacuum oven or by precipitation of a 30wt% dimethylacetamide solution into a four-fold (by mass) excess of a non-solvent (80vol% water/20vol% ethanol). The formulations of the resultant polymer are given in Table 1.

Table 1

Sample	End-Capping Compound	pbw Prepol. 1	pbw BD	pbw End Group
1A1	isocytosine	92.5	5	2.5
1A2	isocytosine	93.0	5.5	1.5
1A3	isocytosine	93.1	5.9	1.0
1B1	6-methyl isocytosine	93.0	5.0	2.0
1B2	6-methyl isocytosine	92.65	5.5	1.85
1B3	6-methyl isocytosine	92.6	5.9	1.5
1C1	2-amino pyrimidine	92.2	4.9	2.9
1C2	2-amino pyrimidine	92.2	5.5	2.3
1C3	2-amino pyrimidine	92.2	5.9	1.9
1D1	ethoxyethoxy- ethanol	88.2	4.7	7.1
1D2	ethoxyethoxy- ethanol	88.9	5.3	5.8
1D3	ethoxyethoxy- ethanol	89.9	5.7	4.4
1D4	ethoxyethoxy- ethanol	90.7	6.3	3.0
1E	None	92.6	7.4	0

- 5 Tensile testing was performed at ambient temperature and a cross-head speed of 100mm/minute on compression-moulded tensile specimens of type S2 (norm DIN53504;

2mm thickness). The results of these tests are recorded in Table 2 (at ambient temperature).

Table 2

Sample	Tensile Strength (Mpa)	%Elongation at Break
1A1	2.66	487
1A2	3.98	655
1A3	7.41	760
1B1	2.32	308
1B2	4.20	618
1B3	7.15	705
1C1	1.51	124
1C2	2.45	211
1C3	3.10	278
1D1	-	-
1D2	1.15	58
1D3	1.77	153
1D4	2.73	212
1 ^E	5.41	553

5

Rheology

The rheological performance of the TPUs was assessed by Rotational Dynamic Shear (RDS) experiments using a Rheometrics RMS800 rheometer.

10

More precisely, RDS rheometry was used to determine the melting behavior and the viscoelastic behavior of the TPUs in the molten state.

The experiments were carried out in the following way.

15

First, a solvent casting (0.5 mm thick) was prepared by dissolving each TPU in DMAc to give approximately a 25 w/w % solution. 160 g of the solution was then degassed and

poured into a flat glass mould in a cool oven. The solvent was then removed by leaving the casting in the oven at 80°C for 24 hours.

Then two 25 mm diameter discs were cut from the solvent casting and inserted under a slight normal pressure between two 25 mm diameter parallel plates to give a 1 mm-thick specimen.

Each experiment was then programmed using the following values :

radius : 12.5 mm
10 frequency : 10.0 rad/s
initial temperature : 40°C
final temperature : 250 °C
step size : 5°C/min
strain : 5%
15 ramp rate : 5
measurement time : 30 s

The viscosities of the polymers in the molten state at 180°C and 200°C are recorded in Table 3.

Table 3

Sample	Melt Viscosity at 180°C (Pa.s)	Melt Viscosity at 200°C (Pa.s)
1A1	3	0.8
1A2	34.5	2.0
1A3	122.5	44
1B1	3.75	08
1B2	9	4
1B3	56	5.5
1C1	2.6	1.9
1C2	18.9	7.7
1C3	77	19
1D1	0.7	0.3
1D2	5	3
1D3	15	5
1D4	95	12
1E	174	34

Example 2

- 5 Prepolymer 1 was synthesised according to the procedure described in Example 1. A pre-calculated amount of a 50wt% solution of Suprasec MPR (Table 3) was then added to a stirred 50wt% dimethylacetamide solution of Prepolymer 1 at 87°C under nitrogen and the reaction continued for 3 hours.
- 10 In the case of Polymer 2A a dimethylacetamide solution of 6-methylisocytosine was added and the resultant reaction mixture heated with stirring at 87°C for 3 hours. After cooling, the polymer was isolated by casting at 50°C in vacuo.

The following table 4 gives the weight composition.

Table 4

Sample	Pbw PPG2000	pbw Suprasec MPR	pbw melso
2A	83.7	14.8	1.5
2B	83.7	16.3	0

Example 3

- 5 Prepolymer 3 was prepared by stirring a mixture of 78.6pbw of a ethyleneglycol / 1,4 butanediol adipate polyester in which the molar ratio of the two glycols amounts 1 to 1 and a hydroxyl value of the polyester amounts to 50 mgKOH/g together with 21.4pbw "Suprasec MPR" at 87°C under nitrogen for three hours. After cooling, the prepolymer was stored as a masterbatch under nitrogen.

10

- A pre-calculated amount of 1,4-butanediol (50wt% solution in dimethylacetamide) was added dropwise over a period of 20 minutes to a known amount of a stirred 50wt% dimethylacetamide solution of the prepolymer at 87°C under nitrogen and the heating/stirring were maintained for a further 3 hours. A dimethylacetamide solution of
- 15 the desired end-capping compound was added to the stirred reaction mixture at 87°C and the reaction conditions were maintained for a further 3 hours. After cooling, the polymer was isolated by casting at 80°C in an oven. The formulations of the resultant polymers are given in Table 5.

Table 5

Sample	End-Capping Compound	pbw Prepol. 3	pbw BD	pbw End Group
3B1	6-methyl isocytosine	92.7	2.6	4.7
3B2	6-methyl isocytosine	93.3	3.0	3.7
3B3	6-methyl isocytosine	93.9	3.3	2.8
3B4	6-methyl isocytosine	95.2	3.9	0.9
3C1	2-amino pyrimidine	93.8	2.6	3.6
3C2	2-amino pyrimidine	94.1	3.0	2.9
3C3	2-amino pyrimidine	94.5	3.4	2.1
3C4	2-amino pyrimidine	95.4	3.9	0.7
3D1	ethoxyethoxy-ethanol	92.4	2.6	5.0
3D2	ethoxyethoxy-ethanol	93.0	3.0	4.0
3D3	ethoxyethoxy-ethanol	93.6	3.4	3.0
3D4	ethoxyethoxy-ethanol	95.1	3.9	1.0
3E	None	95.7	4.3	0.0

Tensile testing was performed at ambient temperature and a cross-head speed of 100mm/minute on solvent-cast tensile specimens of type S2 (norm DIN53504; 0.5mm thickness). The results of these tests are recorded in Table 6.

Table 6

Sample	Elongation at break (%)	Stress at break (Mpa)	Stress at 100% elongation	Stress at 200% elongation	Stress at 300% elongation
3B1	914.39	4.88	2.41	2.76	3
3B2	815.8	11.41	3.04	3.67	4.31
3B3	869.07	17.2	3.21	3.68	4.57
3B4	829.2	18.16	2.95	3.86	4.64
3B5	785.65	21.83	2.88	3.53	4.35
3C1	913.08	4.98	2.21	2.71	3.14
3C2	836.31	16.64	2.58	3.2	4.02
3C3	852.2	17.91	2.55	3.19	4.08
3C4	803.54	26.63	3.01	3.82	5.05
3C5	877.19	16.78	2.64	3.22	3.96
3C6	756.46	3.42	1.99	2.38	2.70
3D1	867	5.52	2.3	2.69	3.13
3D2	801.65	4.94	2.16	2.85	3.29
3D3	713.39	28.63	2.93	3.83	5.06
High molecular weight	715	31.18	2.88	3.71	4.96

Rotational Dynamic Shear (RDS) rheometry was performed on solvent-cast discs (12.5mm radius; 1mm thickness) in temperature sweep mode according to the conditions described in Example 1. The viscosities of the polymers in the molten state at 170oC, 180oC and 200oC are recorded in Table 7.

Table 7

Sample	Melt Viscosity at 180°C (Pa.s)	Melt Viscosity at 200°C (Pa.s)
3B1	34	11
3B2	147	20
3B3	550	89
3B4	46	45
3B5	1500	160
3C1	200	83
3C2	1216	413
3C3	1200	351
3C4	2026	903
3C5	1230	440
3C6	85	17
3D1	210	46
3D2	225	59
3D3	3400	1335
3E	2500	910

Example 4

- 5 Several of the polymers according the invention of Example 1 and new examples 4 (4F1 to 4I1) were tested as adhesives to bond steel to steel. To that aim lap shear test specimen were produced in the following manner. Stainless steel test plates of material type 1.4301 with dimensions of 100 x 25 x 1.5 mm were obtained from Rochell GmbH, Moosbrunn, Germany. Prior to use the test plates were degreased with acetone. The test
- 10 plates were put on a hot plate, which had a temperature between 50 °C. and 150 °C. for at least 2 minutes to increase the temperature of the test plates. In the mean time some polymer was heated above its flow point. To that aim approximately 10 gram of polymer was put in a 125 mL glass jar and heated for at least 15 minutes using an oil bath at a temperature between 60 °C. and 200 °C.. A sufficient amount of molten polymer was
- 15 brought onto a test plate with a metal spatula to slightly overfill the 12.5 x 25 x 0.3 mm joint of the bond. The joint was assembled by positioning the test plates with 12.5 mm

overlap. Subsequently the test plates were slightly pressed together and clamped for about 15 minutes using a universal double clip. For each polymer six specimens were prepared. The lap joint test specimens were conditioned in the lab for at least 2 weeks prior for physical testing. The tensile strength was determined at a crosshead speed of 50 mm/min. and was calculated from the measured tensile force divided by the overlap area. For each series the average value of the tensile strength, its standard deviation and the failure mode were reported and given in Table 8. New examples 4 were made as follows:

10 The polyols used were 1,4 butanedioladipate polyester with an hydroxyl vale of 51 mgKOH/g (polyester A) and 1,6 hexanedioladipate polyester with a hydroxyl value of 30 mgKOH/g (polyester B). The chain extenders (CE) used were tripropylene glycol (TPG), 1,4 butanediol (BD) and 1,6 hexanediol (HD). The isocyanate used was 'Suprasec' MPR. The amine was 6-methylisocytosine, which was finely milled (typical
15 d_{50} = 1.45micron; d_{97} 10micron). As an antioxidant 'IRGANOX' 1010 (antioxidant from Ciba Geigy, IRGANOX is a trademark) was used. The polyester and isocyanate were heated to 80 °C. prior to use. The chain extenders were heated to 60 °C.

The required amounts of polyester, chain extender, isocyanate, amine and antioxidant were weighed into a paper cup and mixed for 1 minute using a 'Heidolph' ('Heidolph' is
20 a trademark) mechanical mixer at 4000 rpm. The total weight of the ingredients, excluding the weight of antioxidant, in all cases amounts to 70 g. The weight amount of 'IRGANOX' 1010 in the mixture always amounted to 0.2g/70 g of reaction mixture. Approximately 50g of the reaction mixture was poured into the mixing chamber of a Brabender Plasticord internal mixer fitted with counter-rotating screws and isothermally
25 heated at 180°C. When the mixture in the mixer had reached temperatures of 180 °C, 0.05g of 'DABCO' S (catalyst from Air Products; DABCO is a trademark) was added to the reacting mixture. The polymerisation was allowed to proceed to completion (typically 2 minutes) and, after cooling, the resultant polymer was removed from the mixer for testing. The residence time of the mixture in the mixer never exceeded 3
30 minutes. The weight amount of reactants for the various polymers is given in the table below.

polymer polyester pbw of polyeste pbw of isocyanate CE pbw of CE pbw of melsc

4F1	A	46.5	16.9 HD	4.5	2.1
4G1	A	46.6	15.2 TPG	6.1	2.1
4G2	A	42.7	17.3 TPG	8.1	1.9
4G3	A	38.5	19.4 TPG	9.6	2.5
4H1	B	38.5	18.7 TPG	11.2	1.6
4I1	A	46.5	17.7 BD	3.7	2.1

Results:

5 Table 8

Polymer	Oil bath temperature (°C)	Plate temperature (°C)	Tensile strength (MPa)	Standard deviation (%)	mode of failure
1A1	200	150	2.9	25	cohesive
1A3	200	150	2.7	20	adhesive
1B1	200	150	2.1	20	cohesive
1B2	200	150	2.5	25	partially cohesive and adhesiv
1B3	200	150	2.7	20	partially cohesive and adhesiv
1C1	200	150	2.5	20	partially cohesive and adhesiv
1C2	200	150	3.1	25	adhesive
1C3	200	150	3.4	30	adhesive
4F1	175	110	4.3	10	adhesive
4G1	165	110	7	10	adhesive
4G1	170	50	7.3	20	adhesive
4G2	170	110	8.2	10	adhesive
4G2	170	70	5.5	20	adhesive
4G3	160	110	8.2	5	adhesive
4H1	160	110	8.7	5	adhesive

Table 9

Polymer	Tensile strength (Mpa)	Standard deviation (%)	Mode of failure
1A1	2.9	25	cohesive
1A3	2.7	20	adhesive
1B1	2.1	20	cohesive
1B2	2.5	25	partially co- and adhesive
1B3	2.7	20	partially co- and adhesive
1C1	2.5	20	partially co- and adhesive
1C2	3.1	25	adhesive
1C3	3.4	30	adhesive

Example 5

- 5 In this experiment a series of polymers were tested which were not according to the invention. These polymers were applied in the same manner as described in Example 4 to prepare the steel/steel lap joints. The results are given in Table 10.

Table 10

Polymer	Tensile strength (MPa)	Standard deviation (%)	Mode of failure
1D2	1.2	15	cohesive
1D3	1.0	30	cohesive
1D4	2.3	15	adhesive
1E	1.9	40	adhesive

10

Example 6

In this experiment a polymer was taken which was not according to the invention. Polymer 2A was applied in the same manner as described in Example 4 to prepare the

steel/steel lap joints. The lap joints thus prepared had no mechanical strength and over time the test plates came apart under gravity.

CLAIMS

1. A process for the preparation of a polymer having the following general formula :



wherein:

PU is a polymer chain comprising at least one polyurethane chain; and

n ranges from 0 to 8;

X, Y and Z, identical or different, are H-bonding sites;

comprising reacting a) a polyisocyanate with a functionality of 2, the polyisocyanate being diphenylmethane diisocyanate, b) a polyol having a MW from 750 to 6000 and a functionality from 1.9 to 2.5, c) a polyol having a MW from 62 to 750 with a functionality of 1.9 to 2.1, and d) an amine compound of formula $\text{H}_2\text{N}-\text{C}(\text{R}_3)=\text{N}-\text{R}_4$, wherein R_3 and R_4 are each independently a C1-C6 alkyl or a C3-C6 cycloalkyl, or together can form a ring having one or two cycle(s), all being optionally interrupted by one or more heteroatom(s), wherein the heteroatom is N, O or S, with a MW less than 400;

wherein the amount of isocyanate a), polyol b), polyol c) and amine d) is 10-50, 35-90, 1-30 and 0.5-20 by weight respectively per 100 parts by weight of isocyanate a), polyol b), polyol c) and amine d), wherein the reaction is conducted at an isocyanate index of 90 to 200.

2. A process as defined in claim 1, wherein the amine compound d) is 2-aminopyrimidine, isocytosine,

6-alkylisocytosine, 2-aminopyridine, 5-amino-uracil
6-tridecylisocytosine, 6-phenylisocytosine,
2-amino-6-(3-butenyl)-4-pyrimidone,
p-di-(2-amino-6-ethyl-4-pyrimidone)benzene,
5 2-amino 4-pyridone, 4-pyrimidone
6-methyl-2-amino-4-pyrimidone,
6-ethyl-2-amino-4-pyrimidone,
6-phenyl-2-amino-4-pyrimidone,
6-(p-nitrophenyl)isocytosine,
10 6-(trifluoromethyl)isocytosine or any mixture thereof.

3. A process as defined in claim 2, wherein the amine compound d) is 6-methylisocytosine.

15 4. A process as defined in claim 1, wherein the PU is a thermoplastic and/or an elastomeric polyurethane.

5. A process as defined in claim 1, wherein said polyurethane chain has an average molecular weight in the
20 range 2000 to 50000.

6. A process as defined in claim 1, wherein said polyurethane chain has an average molecular weight in the
range 5000 to 40000.

25

7. A supramolecular polymer comprising units that form H-bonds with one another, wherein at least one of these units is a polymer obtained by a process as defined in any one of claims 1 to 6.

30

8. Use of a supramolecular polymer as defined in claim 7 as an hot melt adhesive.

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9. Use of a supramolecular polymer as defined in claim 7 in rotational or slush molding.

10. Use of a supramolecular polymer as defined in claim 7 in
5 injection molding.

11. Use of a supramolecular polymer as defined in claim 7 in the manufacture of TPU foams.

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