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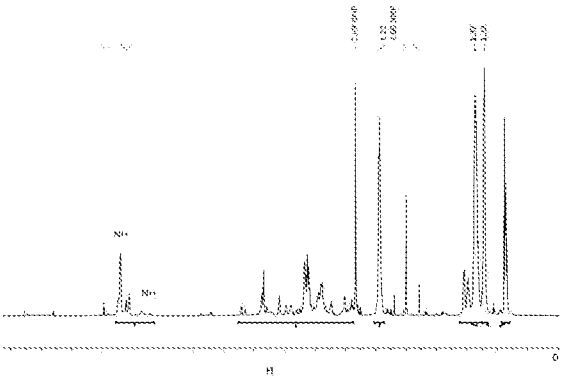
(54) METHOD FOR MODIFICATION OF POLY(HYDROXYUERETHANES) (PHUs).

(57) The invention relates to a process for preparing a modified polyhydroxyurethane (PHU) comprising the step of: reacting a starting non-modified PHU compound, having repeating units, containing two proximate hydroxyl groups separated by 2 to 7 atoms, with a chemical capable of ring formation with the hydroxyl functionalities, selected from the group consisting of an aldehyde compound, ketone compound and boronic acid compound, in the presence of a Bronsted acid type catalyst, and a solvent, and using a stoichiometric ratio of said aldehyde, ketone, boronic acid compounds to the repeating unit of polymer (I) of between 0.1:1 and 100:1 by mol, at a temperature range of from 40°C to 100°C, during 24h-96h.

[Fig 1a)]



Method for modification of poly(hydroxyurethanes) (PHUs)

The invention relates to the field of non-isocyanate polyurethanes (NIPU). More specifically the invention relates to a process for modifying NIPU to provide them with specific targeted properties.

Polyurethanes (PU) are produced by reacting diisocyanates with polyols in the presence of a catalyst or without it, or upon exposure to ultraviolet light. Common catalysts include tertiary amines, such as triethylamine (TEA), tetrametylethylenediamine (TE), pentamethyldiethylenetriamine (DT), 1,5,7-triazobicyclo[4.4.0]dec-5-ene (TBD), 1,4-diazabicyclo[2.2.2]octane (DABCO), etc. or metallic soaps, such as dibutyltin dilaurate or tin(II) 2-ethylhexanoate. The stoichiometry of the starting materials must be carefully controlled as excess isocyanate can trimerize, leading to the formation of rigid polyisocyanurates. The moisture content should be also managed as the traces of water start to convert the isocyanates to amines, while the latter immediately react to form urea linkages with simultaneous release of gaseous CO_2. As a result, the polymer usually has a highly crosslinked molecular structure, resulting in a thermosetting material which does not melt on heating; although some thermoplastic polyurethanes are also produced.

Use of isocyanate-based monomers in PU synthesis indeed raises severe health concerns. Regular isocyanates are actually synthesized using phosgene, a highly reactive and toxic gas. Isocyanates themselves are very toxic and powerful irritants to the mucous membranes of the eyes as well as to gastrointestinal and respiratory tracts. Direct skin contact can also cause significant inflammation. Isocyanates are known to cause chronical asthma issues and can also sensitize workers, making them subject to severe asthma attacks if they are exposed again. Moreover, PU synthesis most often requires the use of a catalyst, typically organotin compounds, such as dibutyltin dilaurate or tin(II) 2-ethylhexanoate. The success of this catalyst is related to its high activity at low loading. However, it can be hardly removed from the final polymers. The presence of residual catalyst in PUs causes detrimental effects on their aging. In addition, some studies suggested the possibility of tissue function endangerment through slow penetration of the catalyst into the blood circulation system, which questions the usage of tin-derived PUs in biomedical and food contact applications. Finally, as PUs are usually synthesized in organic solvents, for a use in applications such as coatings, paints, inks and adhesives, this necessitates the evaporation of a large amount of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) in the atmosphere. Exposure to VOCs are known to provoke health effects, such as headaches, dizziness, irritation, cancer, and the like. Thus, researchers in industry and in academia have put significant efforts in the past years to find synthetic alternatives to PUs, involving non-toxic reagents.

One of these alternatives consists in the synthesis of non-isocyanate polyurethanes, referred to as NIPUs. One can distinguish seven synthetic pathways to NIPUs, including (1) the step-growth polymerization of bis-cyclic carbonates and diamines, (2) the step-growth polymerization of linear activated dicarbonates and diamines, (3) the step-growth polymerization of linear activated bis-carbamates and diols, (4) the step-growth polymerization of alkylene bis-ureas and diepoxides, (5) the self polycondensation of bis-hydroxyalkylcarbamates, (6) the self polycondensation of AB-type synthons (R'-O-CO-NH-R-OH, for example), and (7) the ring-opening polymerization of cyclic carbamates. NIPU has attracted increasing attention because of the much "greener" synthetic routes not involving highly toxic compounds and their potential to substitute conventional PUs. Their potential technological applications include chemical-resistant coating, sealants, foam, etc. (Jing Guan et al, Progress in Study of Non-Isocyanate Polyurethane, *Ind. Eng. Chem. Res.* 2011, 50, 11, 6517–6527; Amaury Bossion, PhD thesis, december 18, 2018, "New challenges in the synthesis of non-isocyanate polyurethanes").

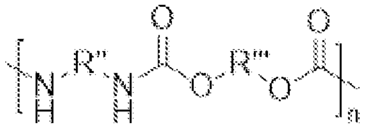
The most common type of NIPUs are the polyhydroxyurethanes (PHUs) which contain at least two secondary hydroxyl groups in each repeating unit as the consequence of their synthesis. These materials suffer from being highly hydrophilic, impairing their mechanical properties, i.e. there is a high dependence of mechanical properties on humidity. In addition, this tendency to absorb moisture can result in in hydrolysis when the materials are heated leading to the loss of the molecular weight and significantly lowering of mechanical properties and physical stability in humid atmosphere. Moreover, the absorbed water due to the presence of high amounts of hydroxyl groups can act as the plasticizer significantly reducing the glass transition temperature of PHUs and drastically decreasing the mechanical properties on storage or in humid atmosphere.

The literature has reported that the mechanical properties of the modified PHUs are usually lower compared to unmodified ones due, for example, the introduction of polymeric side chains or short-chained substituents that results in loss of intermolecular hydrogen bonding.

Accordingly, there is a need to provide modified PHUs that (i) are presenting reduced water sensitivity (or improved hydrophobicity), (ii) are retaining the mechanical properties of linear unmodified PHUs, and/or (iii) are presenting high tolerance towards the introduced functionality allowing then a large selection of new properties, such as luminescence, fluorescence, gas sorption ability, hydrophobicity, UV curability, etc.

The invention relates to a process for preparing a modified polyhydroxyurethane (PHU) comprising the step of:

reacting a starting non-modified PHU compound, having repeating units, containing two proximate hydroxyl groups separated by 2 to 7 atoms, of formula (I)



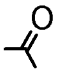
(I)

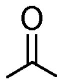
wherein

R'' is derived from a diamine reagent and is comprised of one or more of the following entities selected from the group consisting of: linear or branched aliphatic, cycloaliphatic and aromatic moeities, oligomeric/(co-)polymeric species, such as poly(alkylene oxides), poly(siloxanes), poly(dienes), poly(olefins), poly(amides), and (co-)polymeric species in the form of amine-terminated oligomers;

R’’’ is derived from a dicarbonate reagent which consists of terminal carbonate groups, and is comprised of one or more of the following entities selected from the group consisting: linear or branched aliphatic, cycloaliphatic, and aromatic moieties; and additionally, that contains at least 2 hydroxyl functionalities (-OH), said hydroxyl functionalities being separated by no more than 7 atoms;

with a chemical capable of ring formation with the hydroxyl functionalities, selected from the group consisting of an aldehyde compound of formula (II), ketone compound of formula (III) and boronic acid compound of formula (IV)


(II)


(III)


(IV)

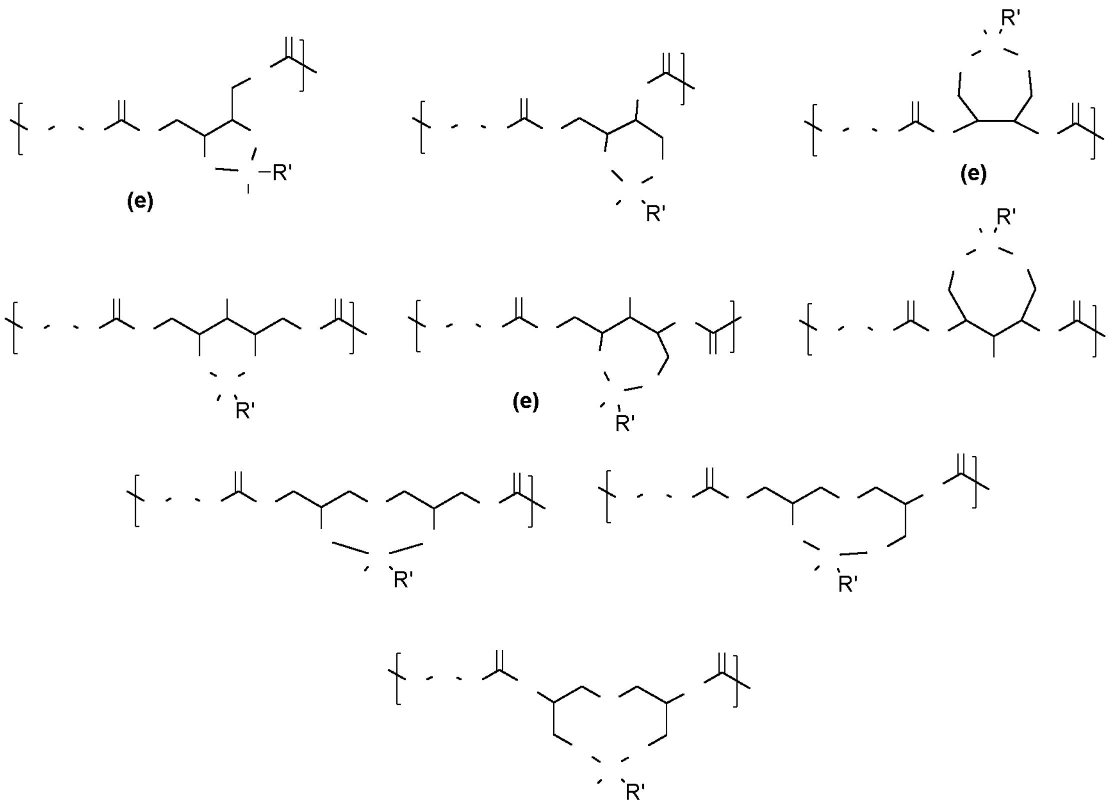
in the presence of a Bronsted acid type catalyst, and a solvent, and using a stoichiometric ratio of compound (II), (III), and / or (IV) to the repeating unit of polymer (I) of between 0.1:1 and 100:1 by mol, at a temperature range of from 40°C to 100°C, during 24h-96h,

wherein

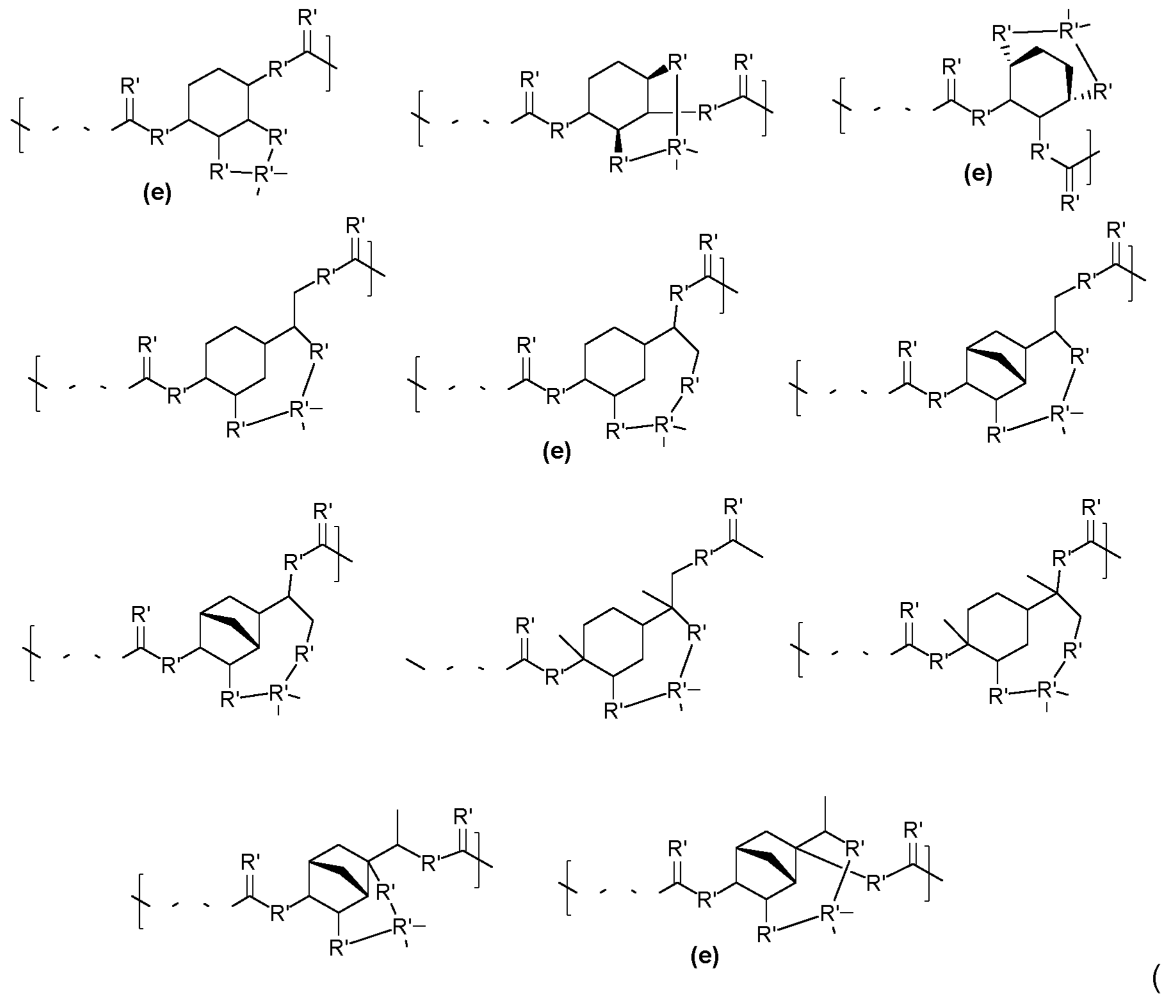
- n, is integer of from 5 to 150;
- R, R’ are, independently, selected from the group consisting of a linear or branched C_1-C_{10} alkyl or alkoxy group; a linear or branched C_2-C_{10} alkenyl or alkylenoxy group; a linear or branched C_2-C_{10} alkynyl group; a cyclo(C_3-C_6 alkyl) group; a heterocyclo(C_3-C_6 alkyl) group, wherein the hetero atom is selected from N, S, and O; at least one linear or branched C_1-C_6 alkyl group, C_2-C_6 alkenyl or alkylenoxy group, a linear or branched C_2-C_6 alkynyl group, $(CH_2)_m$-Ar group, where Ar is any aromatic ring or condensed aromatic ring, additionally substituted or unsubstituted, optionally including heterocycles, -$(CH_2)_m$-CF_3 group, -CH_2-$(CF_2)_m$-CF_3 group, o-, m-, p- substituted or unsubstituted phenyl group, polycyclic aromatic (PAH), heteroaromatic hydrocarbon and a keto heteroaromatic hydrocarbon, wherein m is of from 0 to 6.

The Applicant has shown that the modified poly(hydroxyurethanes) (PHUs) of the invention are, in the context of the invention, aldehyde modified PHUs, ketone modified PHUs and boronic acid modified PHUs.

Advantageously, the process is leading to modified poly(hydroxyurethanes) (PHUs) which are, for example, presenting a non limitative isomeric linear structure of formula (V) and/or a cycloaliphatic structure of formula (VI), selected preferably from the group consisting of



(V)



(VI)

The process of the invention may in some other words result in modified PHU(s) (aldehyde modified PHU(s), ketone modified PHU(s) and boronic acid modified PHU(s)) by forming a ring through the reaction of two proximate hydroxyl groups, i.e. separated by 2 to 7 atoms, preferably 2 to 5 carbon atoms, more preferably 2 to 4 carbon atoms, where the substructure O-X-O is formed, where the O atom is derived from approximate hydroxyls and X represents a single atom coming from the chemical capable of ring formation with the hydroxyl functionalities, here also named modification agent.

In some preferable embodiments, the starting non-modified PHU compound of formula (I) may advantageously be selected to lead to modified PHU(s) exhibiting Mw values greater than 5 000 Da, better greater than 7 500 Da, and especially greater than 10 000 Da. In some aspects the Mw values may be of from 5 000 to

20 000 Da. Advantageously, it is highly desirable that the Mw values are above the entanglement molecular weight.

The main advantage of the process is the manufacture of aldehyde modified PHU(s), ketone modified PHU(s) and boronic acid modified PHU(s) exhibiting a reduced water adsorption (expressed in %).

Typically, the water adsorption is measured at various humidity environment, such as in a closed space, for example, a constant climate chamber or an experimental room, wherein the temperature and the humidity are maintained constant and defined as being for example a room humidity (45%) and/or 65%-85% humidity. The precise humidity measurement is realised either with electronic humidity controller or with a psychrometer in accordance with ASTM E337-15 standard.

Globally, the water adsorption (in wt.%) of the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s), is found to be essentially constant from about 10 days. “Essentially” means, in the context of the invention, that the variations (deviations) of water adsorption are within the range of about 0,1-0,2 wt.%. Typical values are, at room humidity (45%), less than 1,5 wt.%, preferably from 0,1 to 1 wt.%, better from 0,2 to 1 wt.%, said values being essentially constant after about 3 days of the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) exposition. When compared to starting non-modified PHU(s), the latter exhibit a value of at least 2 wt % of water adsorption, said value being constant and obtained after at least 8 days of exposition to the humidity.

Same tendency is observed when experiments are performed under 65% of humidity (same experimental conditions). Typical values are, at 65% of humidity, from 0,8 to 2,3 wt.%, better from 1,0 to 2,0 wt.%, said values being essentially constant after about 7 days of the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) exposition to humidity. When compared to starting non modified PHU(s), the latter exhibit a value of at least 3,5 wt.% of water adsorption, said value being essentially constant and obtained after at least 9 days of exposition to the humidity.

Experiments performed under 85% of humidity (same experimental conditions) show values of preferably from 2,1 to 4,3 wt.%, better from 2,3 to 4,0 wt.%, said values being essentially constant after about 9 days of the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) exposition. When compared to starting non modified PHU(s), the latter exhibit a value of at least 7,5 wt % of water adsorption, said value being essentially constant and obtained after at least 6 days of exposition to the humidity.

In some alternate embodiments, the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) are exhibiting a water adsorption (in wt %) which is reduced of at least 70% as compared to the starting non modified PHU(s) , preferably the water adsorption being reduced from 1,7 to 10 fold with comparison to the starting non modified PHU(s), at same experimental conditions. For example, at room humidity, up to 5-fold water adsorption reduction may be observed; at 65% and 85% of humidity, up to 4-fold water adsorption reduction may be observed.

The process allows to obtain the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s), from a starting non modified PHU, which are exhibiting degrees of modification of at least 75%, preferably of from 75% to 95%, better of from 80% to 92%.

Another improved properties of the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) obtained through the process is (i) the maintenance of mechanical properties and (ii) reduced dependence of the mechanical properties on humidity in comparison with the starting non modified PHU(s), at same experimental conditions.

The dependence of the mechanical properties on humidity of the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) in comparison with the starting non modified PHU(s), at same experimental conditions, may be within the range of 50-120 fold lower.

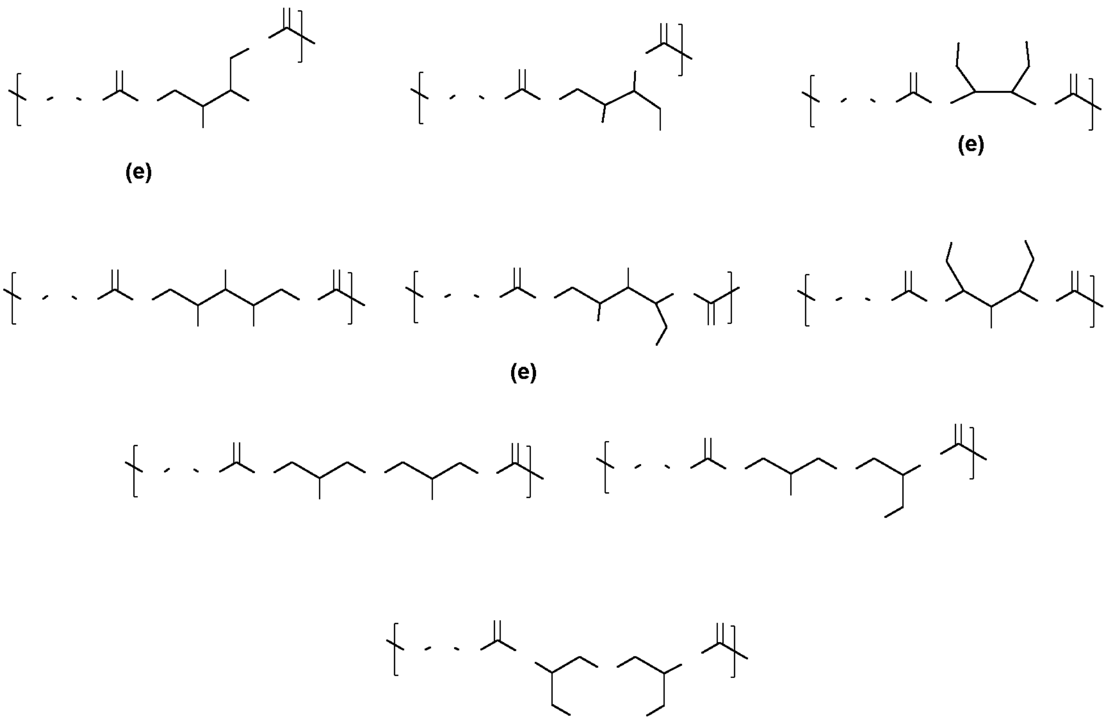
For example, a graph related to the variation of the storage modulus (Pa) vs frequency (Hz) for starting non modified PHU(s), measured in accordance with the ASTM D5279-21 standard, at room humidity (45%), 65% and 85% humidity respectively, shows high range values of the storage modulus within the frequency range of 0,5 Hz-20 Hz, typical respective values may be within the range 1700.10^7 to 5,4.10^7 Pa (variations of about 315 fold). For the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) obtained through the process, typical respective values may be within the range of 43.10^7 to 7,4.10^7 Pa (variations of about 6 fold), or 53.10^7 to 20.10^7 Pa (variations of about 2.60). These values of the storage modulus (Pa) vs frequency (Hz) show that that the mechanical properties are maintained within the same order of magnitude.

The obtained aldehyde modified PHU(s) very advantageously exhibit a higher contact angle, for example, increased of about 5-36% in comparison with the starting non modified PHU(s), at same experimental conditions, demonstrating the increased hydrophobicity.

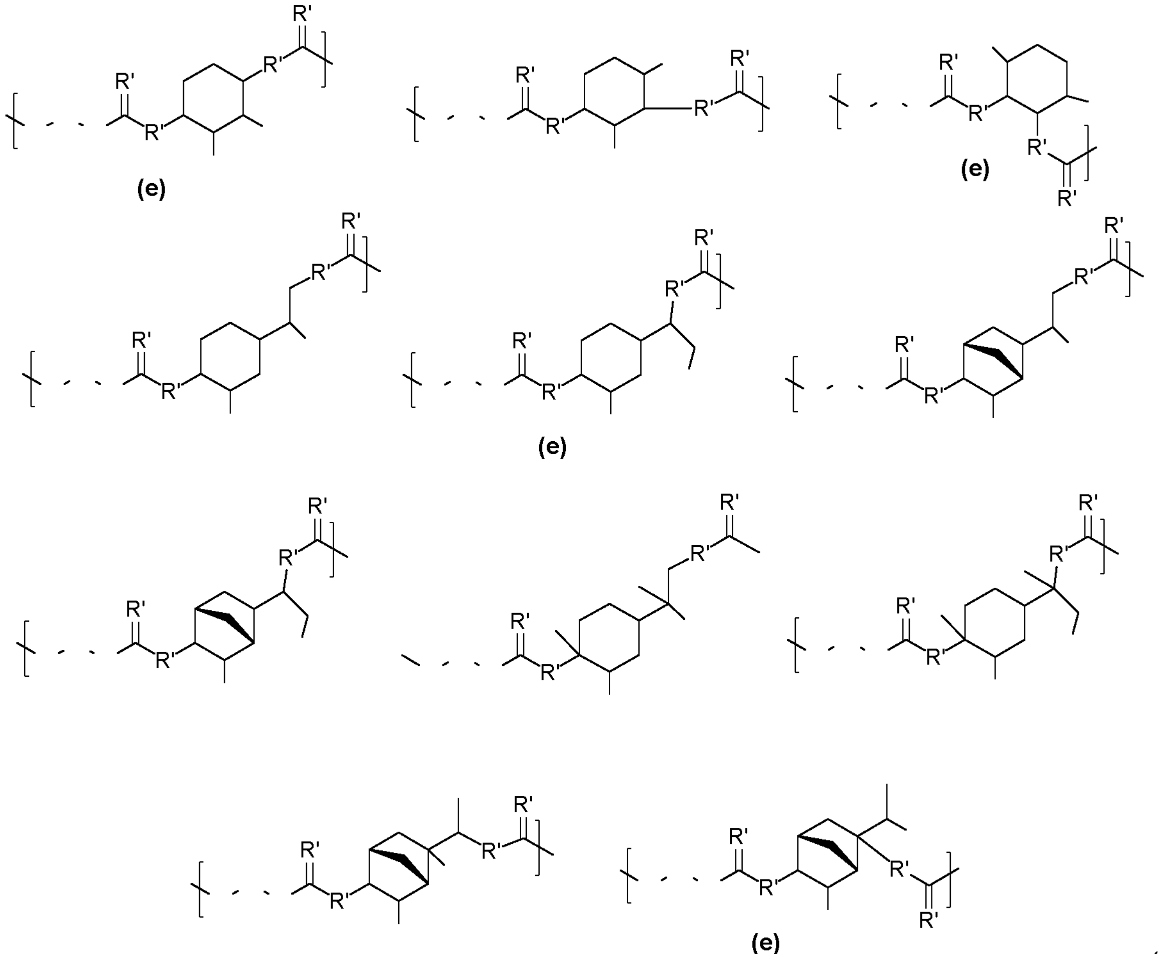
With the use of some specific aldehydes in the process, the aldehyde modified PHUs may exhibit some fluorescence or luminescence properties. This is especially the case when 4-butanal-8-hydroxycumarine is used.

Also, bio-based non modified PHU(s) are preferably used.

Advantageously, the neat non-modified PHU compound of formula (I) may be an isomeric linear PHU of formula (Ia) and/or a cycloaliphatic PHU of formula (Ib)



(Ia)



(Ib)

wherein R” and n have the same meanings as above defined.

The process is carried out in the presence of a Bronsted acid type catalyst, being preferably selected from p-toluenesulfonic acid (p-TCA), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), methanesulfionic acid (CF_3SO_3H), tetrafluoroboric acid (HBF_4) and hexafluorophosphoric acid (HPF_6), and mixtures thereof.

The Bronsted acid type catalyst may be used at 4-56 mol% of loading calculated per a repeating polymer unit.

The process is performed with the use of a solvent. Preferred solvents may be n-methyl-2-pyrrolidone (NMP), N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAc), Dimethyl sulfoxide (DMSO) or any other polar solvent capable to dissolve the starting non modified PHU(s).

The temperature range of the process, 40°C to 100°C, is selected to avoid any degradation of the stating non-modified PHU(s), for example, the urethane linkage that may cause reversion to an unwanted isocyanate plus a hydroxyl compounds.

The selected duration time of the reaction is of from 24h to 96h, and, without being bound by any theory, may be depending on the removal or not of the water formed, as side product, and/or whether the aldehyde or ketone is activated by presence of a certain functional groups or not.

The preferred temperature may be within 60°C to 90°C, and duration may be within 24h to 85h, which are the most preferable ranges for optimally avoid the drawbacks previously cited.

Preferably, R and R', independently, are selected from the group consisting of a linear or branched C_1-C_8 alkyl or alkoxy group; a linear or branched C_2-C_8 alkenyl or alkylenoxy group; a linear or branched C_2-C_8 alkynyl group; a cyclo(C_3-C_6alkyl) group; a heterocyclo(C_3-C_6alkyl) group, wherein the hetero atom is selected from N, S, and O; at least one linear or branched C_1-C_6 alkyl group, C_2-C_6 alkenyl or alkylenoxy group, a linear or branched C_2-C_6 alkynyl group, -$(CH_2)_m$-Ar group, where Ar is any aromatic ring or condensed aromatic ring, additionally substituted or unsubstituted, optionally including heterocycles, such as O, N, S, -$(CH_2)_m$-CF_3 group o-, m-, p- substituted or unsubstituted phenyl group, polycyclic aromatic (PAH), heteroaromatic hydrocarbon and a keto heteroaromatic hydrocarbon, wherein m is of from 0 to 4, such as 4-butanal-8-hydroxycumarine and HOC-$(CH_2)_m$-Ar preferably selected form α-tolyaldehyde, cinnamaldehyde and hydrocinnamaldehyde.

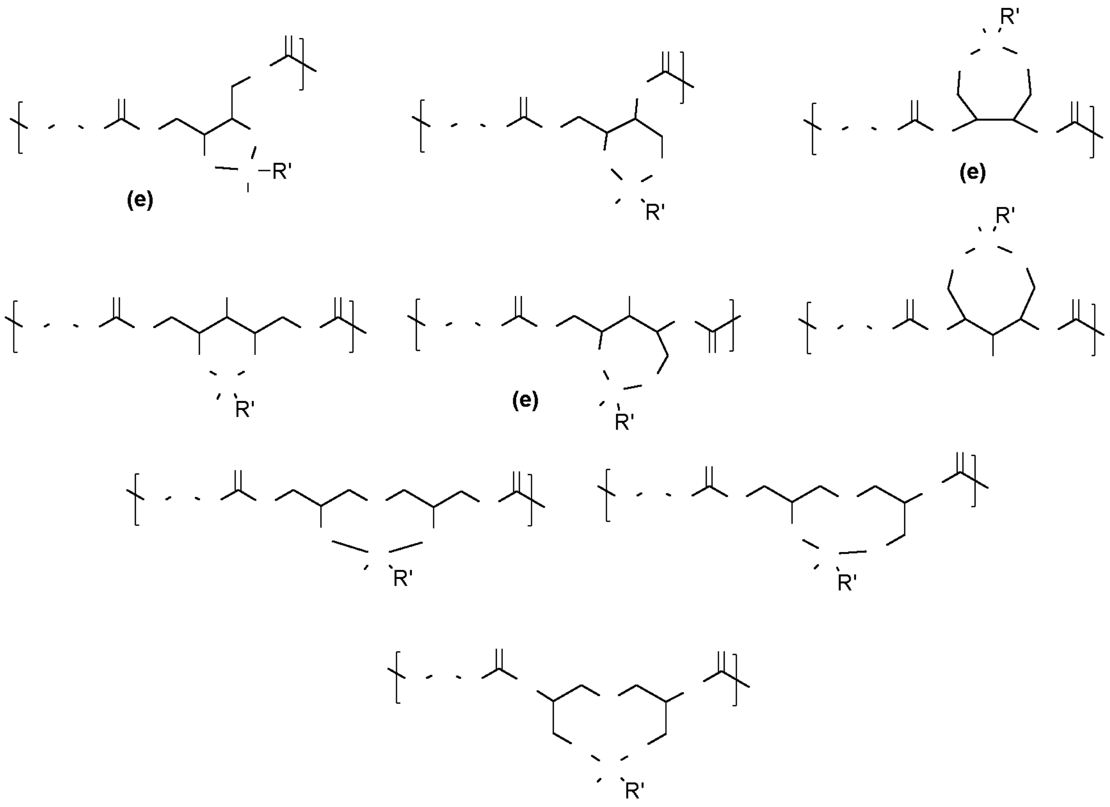
When the R group of compounds of formula (II) to (IV) is a phenyl group, polycyclic aromatic (PAH), heteroaromatic hydrocarbon and a keto heteroaromatic hydrocarbon, these may be substituted in ortho, meta and/or para position in the ring.

The neat non modified PHU(s) used as the starting material for the aldehyde modified PHU(s), ketone modified PHU(s) or boronic acid modified PHU(s) is/are synthesized through known step-growth polymerization of respective bis-cyclic carbonates and di-amines (see Amaury Bossion cited above).

In some examples, the diamine reagent (defined for R”) may be hexamethylenediamine (HMDA and the like, the dicarbonate reagent may be 1,2;3,4-erythritol dicarbonate and 4-vinylcyclohexene dicarbonate.

Additionally, non-limitative examples of compound (II) may be butyraldehyde, heptaldehyde, p-trifluoromethylbenzaldehyde, 3-phenylpropanal, compound (III) may be benzophenone, acetone and compound (IV) may be phenylboronic acid.

The invention also relates to modified poly(hydroxyurethanes) (PHUs) obtainable by the process of the invention presenting an isomeric linear structure of formula (V) and/or a cycloaliphatic structure of formula (VI) selected from the group consisting of



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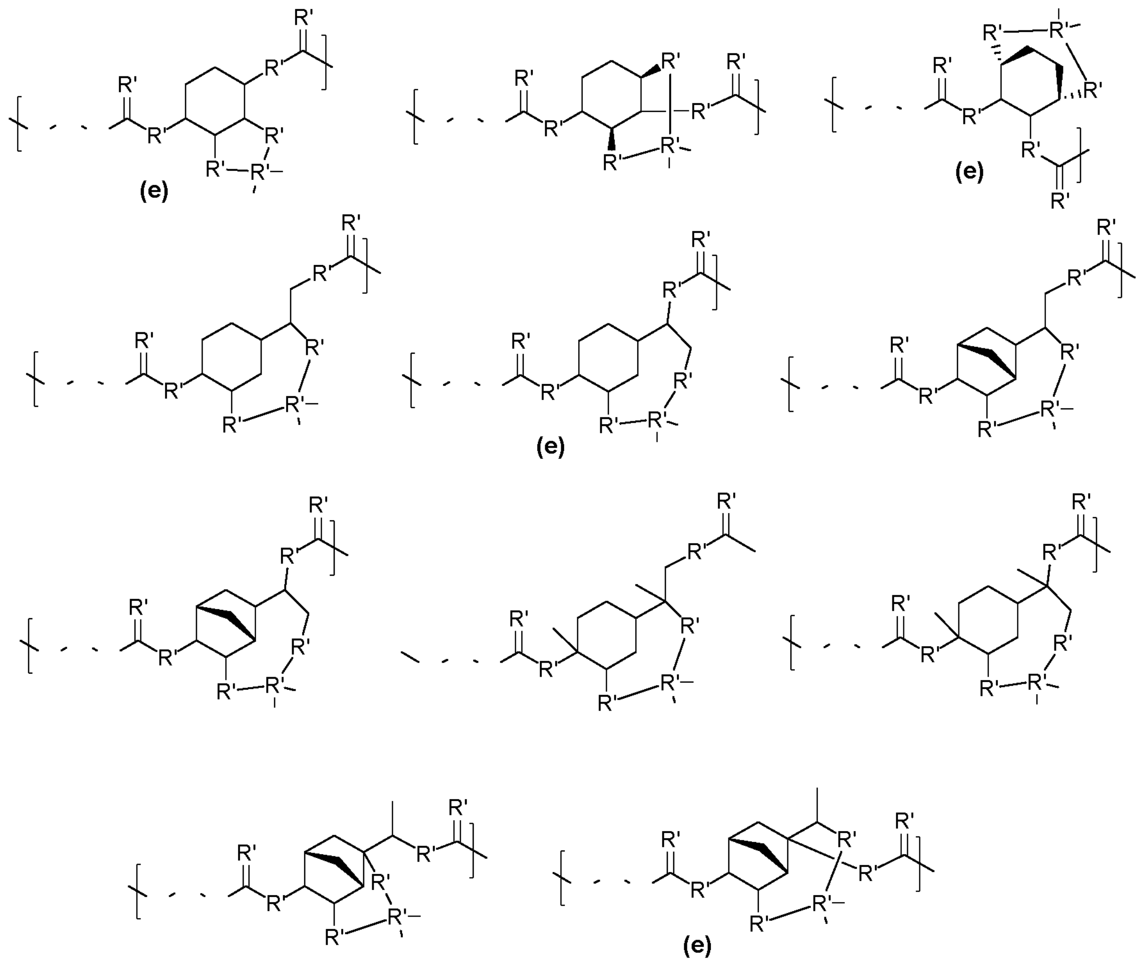


(VI)

wherein R, R’, R” and n have the same meanings as above defined.

The modified poly(hydroxyurethanes) (PHUs) exhibit all the properties listed above.

In some embodoments, the modified poly(hydroxyurethanes) (PHUs) may exhibit modification degrees in the range of 75-95% (determined by NMR), preferably of from 80 to 85%, in comparison to a starting non-modified PHU compound.

In some alternate embodiments, the modified poly(hydroxyurethanes) (PHUs) may exhibit modification degrees in the range of 50-60%,

The invention will be described in some more details with accompanying figures.

Figures 1a) and 1b) represent respectively the ^1H NMR and ^{13}C NMR of the modified PHU-compound A- of Example 1 obtained according to an embodiment of the invention.

Figures 2a) and 2b) represent respectively the ^{1}H NMR and ^{13}C NMR of the modified PHU-compound B- of Example 2 obtained according to an embodiment of the invention.

Figures 3a), 3b) and 3c) represent respectively the ^{1}H NMR,^{13}C NMR and ^{19}F NMR of the modified PHU-compound C- of Example 3 obtained according to an embodiment of the invention.

Figures 4a) and 4b) represent respectively the ^{1}H NMR and ^{13}C NMR of the modified PHU-compound D- of Example 4 obtained according to an embodiment of the invention.

Figure 5 represents the ^{1}H NMR of the modified PHU-compound E of Example 5 obtained according to an embodiment of the invention.

Figure 6 represents the ^{1}H NMR of the modified PHU-compound F of Example 6 obtained according to an embodiment of the invention.

Figure 7 represents Storage Modulus (measured using rheology) plots of PU control, PHU1 control, Compound D and Compound C measured at different humidity levels (45, 65 and 85%)

Mechanical properties of PHU samples, i.e., σ_t - tensile strength (kPa), E_t - tensile modulus (MPa) and ε - elongation (%) are measured at room temperature using a universal test machine Instron 5967 (Norwood, MA, USA) equipped with a load cell of 1 kN according to ASTM D882-18 and D638-14. The measurements were achieved at a crosshead speed of 5 mm/min. Before tests, samples were bar-shaped (40 × 10 × 2 mm) by using vacuum compression moulding MeltPrep (MeltPrep GmbH, Austria) machine at 90°C for modified PHU samples and at 120°C for non-modified ones under 1 mbar vacuum according to ASTM D4703 standard and stored during 72 h in the specified humidity conditions (45, 65 and 85%). At least 5 specimens were tested per reference.

The surface wettability of the aldehyde modified and control PHU(s) was measured in accordance with the ASTM D7334-08(2022) standard. The water contact angle (CA) measurements were performed using the sessile drop method on a Contact

Angle System OCA (Apollo Instruments, France), at 25˚C and atmospheric pressure. A 10 µL drop of deionized water (MilliQ purity) was released through a motor-driven syringe onto the surface of the tested PHU film. The photo image of the drop was acquired after 15 seconds after the drop placement by a numerical camera and transmitted to a computer workstation to calculate the contact angle. The contact angles were calculated using SCA 20 v.2 software using automatic profile analysis protocol. Each reported value is the average of at least six independent measurements. The standard deviation due to experimental error was estimated to be approximately 2%.

Water adsorption was measured for each polymer sample using bars (typical length x width x thickness = 20 x 5 x 1.5 mm) at three humidity conditions: 45 (room humidity), 65 and 85% controlled according to ASTM E337-15. The water adsorption was calculated using formula:

The W.a. (%) = Weight of bar (stored at specified humidity for xh)/ Weight of bar (right after preparation) x 100%

The increase of the weight of each sample was recorded each 24h for 1st three days and then each 72h till 15th day.

NMR spectra were recorded on AMX-600 spectrometer (Bruker, Germany) at 25°C in the indicated deuterated solvent and are listed in ppm. The signals corresponding to the residual protons and carbons of the deuterated solvent were used as an internal standard for ^{1}H and ^{13}C NMR, respectively. The C_6F_6 was utilized as an external standard for ^{19}F NMR, while the $F_3B{\cdot}OEt_2$ was used as an external standard for ^{11}B NMR, respectively.

Thermal gravimetric analysis (TGA) of polymer samples was performed in accordance with ASTM E2550-17 standard. TGA was carried out in air on a TGA2 STARe System (Mettler Toledo, Switzerland) applying a heating rate of 5°C/min. The onset weight loss temperature (T_{onset}) was determined as the point in the TGA curve at which a significant deviation from the horizontal was observed. The resulting temperature was then rounded to the nearest 5°C.

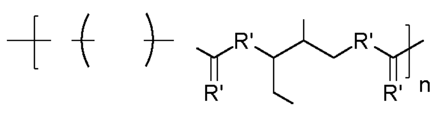
Differential Scanning Calorimetry (DSC) was performed in accordance with ASTM D3418-21 standard. Samples were hermetically sealed in Al pans on air and DSC analysis was performed on a DSC3+ STARe System (Mettler Toledo, Switzerland) differential calorimeter applying a heating rate of 10°C/min in the range of -80°C to 190°C. The glass transition (T_g) was determined during second heating cycle.

Dynamic Mechanical Thermal Analysis (DMTA) was performed in accordance with the ASTM D7028-07 standard. Measurements were carried out on bars (typical length x width x thickness = 20 x 5 x 2 mm) with a DMA 242 C model (Netzsch, Germany) operating in tension mode (strain between 0.75 and 1.25 %, pretension: 8 N). Experiments were performed at 1 Hz frequency with a heating rate of 2°C/min from -50 to 120°C. The set up provided the storage and loss moduli (E' and E"). The damping parameter or loss factor (tan δ) was defined as the ratio tan δ = E"/E'.

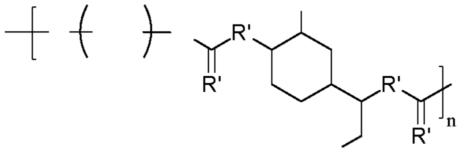
Rheology measurements were performed in torsion mode with bar geometry using an Anton Paar Physica MCR 302 rheometer equipped with a CTD 180 temperature control device and a humidity controller MHG100. Polymer samples in a form of bars (typical length x width x thickness = 20 x 5 x 1.5 mm) were stored during 72 h in the specified humidity conditions (45, 65 and 85%) before measurement and then loaded directly in the clamping system. The samples were tested in accordance with ASTM D5279-21 standard in frequency sweep mode from 0.1 to 100 Hz and at an imposed 0.1% shear strain, ensuring that both moduli G′ and G″ were obtained in the linear viscoelastic regime. All measurements were carried out at 25°C and constant humidity (45, 65 or 85%) maintained by MHG100 humidity controller. Tests were repeated at least twice to insure good repeatability of the results.

Examples

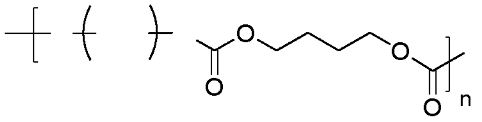
In the examples, the following compounds are defined, as neat (starting) PHUs or non-modified PHUs



PHU1



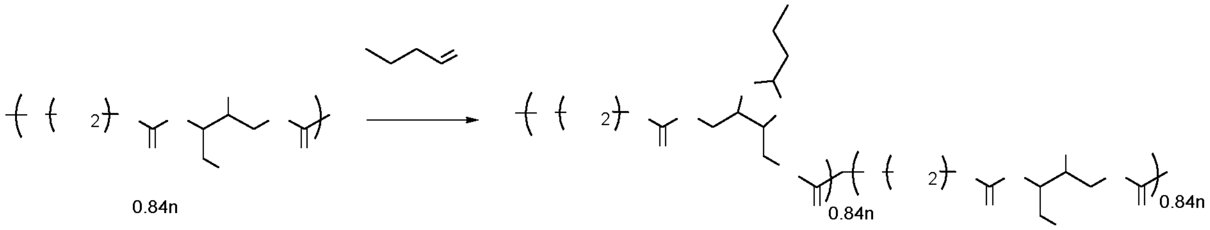
In the examples, the following compound is defined, as PU.



It was used as a reference for comparison of properties of modified and non-modified PHUs with regular PU possessing the most similar structure.

Example 1

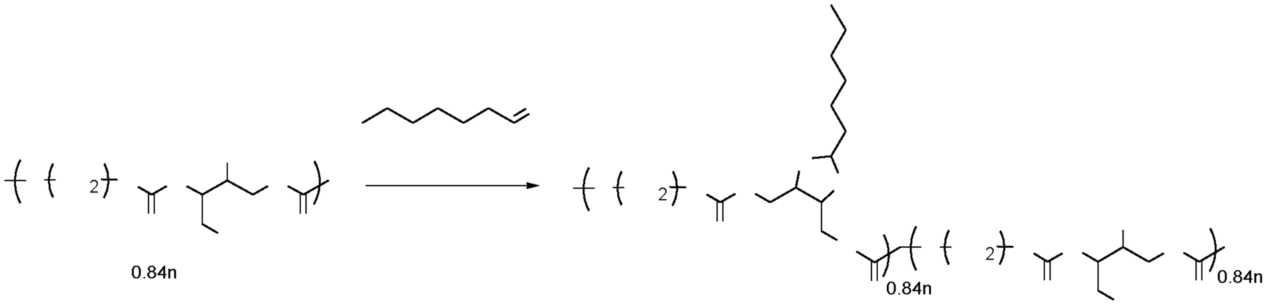
The following synthesis of a modified PHU was performed (Compound A).



The PHU1 polymer (10.0 g, 34.48 mmol) derived from 1,2:3,4-erythritol dicarbonate (BDC) and hexamethylenediamine (HMDA) was placed in a 250 ml round bottom flask equipped with magnetic stirrer. Then the flask was closed with septum, evacuated, and filled with argon. The 80 ml of anhydrous N-methyl-2-pyrrolidone was added to the flask using syringe and the polymer was dissolved over 1 hour at 70°C with continuous stirring. Then the solution of a catalyst – p-toluenesulfonic acid (p-TSA) (2.489 g, 13.1 mmol) in 5 ml of anhydrous N-methyl-2-pyrrolidone was added and stirred over 5 minutes. Finally, butyraldehyde (14.0 g, 194.14 mmol) was added via syringe and the reaction mixture was stirred at 70°C for 72 h. After the completion of the reaction triethylamine (3 ml) was added to the mixture to quench the catalyst and the flask was cooled down to room temperature with stirring for 1 hour. The polymer was precipitated into water, isolated by filtration, redissolved in tetrahydrofuran (THF) and precipitated into the excess of diethyl ether. The precipitated polymer was isolated by filtration and dried at 80˚C/1-2 mbar for 10 h. Yield: 9.4 g (79.2 %). Modification degree (calculated from ^{1}H NMR): 84%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.28 – 6.65 (m, 2H), 5.26 – 3.37 (m, 7H), 2.94 (s, 4H), 1.62 – 1.25 (m, 8H), 1.22 (s, 4H), 0.91 – 0.81 (m, 3H). ^{13}C NMR (151 MHz, DMSO) δ 156.50, 155.90, 155.77, 154.90, 145.85, 137.52, 128.01, 125.50, 104.01, 103.22, 100.79, 100.64, 79.71, 76.78, 74.93, 74.81, 70.25, 69.94, 67.34, 65.79, 63.37, 62.71, 61.91, 60.91, 48.49, 40.76, 40.21, 40.06, 36.15, 35.98, 35.80, 35.61, 35.23, 30.10, 30.02, 29.41, 29.32, 29.17, 28.99, 25.99, 25.95, 25.91, 24.69, 24.43, 17.22, 17.07, 17.02, 16.96, 16.92, 16.84, 16.73, 14.32, 13.95, 13.88, 13.81, 13.77. T_g (DSC, 10˚C/min): 35 ˚C. T_{onset} (TGA, 5˚C/min): 185 ˚C. Anal. Calcd. for $C_{15.32}H_{26.98}N_2O_6$: C, 54.89 %; H, 8.11 %; N, 8.36 %; Found: C, 55.02 %; H, 8.00 %; N, 8.20 %.

Example 2

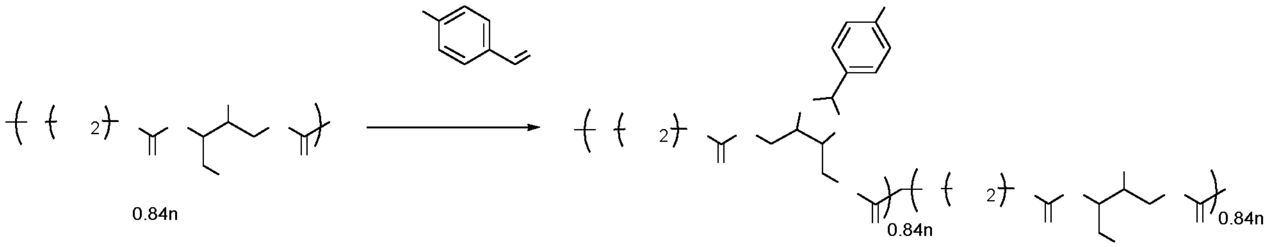
The following synthesis of a modified PHU was performed (Compound B).



The PHU1 polymer (9.5 g, 32.76 mmol) derived from 1,2:3,4-erythritol dicarbonate (BDC) and hexamethylenediamine (HMDA) was placed in a 250 ml round bottom flask equipped with magnetic stirrer. Then the flask was closed with septum, evacuated, and filled with argon. The 80 ml of anhydrous N-methyl-2-pyrrolidone was added to the flask using syringe and the polymer was dissolved over 1 hour at 70˚C with continuous stirring. Then solution of a catalyst – p-toluenesulfonic acid (p-TSA) (2.365 g, 12.44 mmol) in 5 ml of anhydrous N-methyl-2-pyrrolidone was added and stirred over 5 minutes. Finally, heptaldehyde (21.06 g, 184.43 mmol) was added via syringe and the reaction mixture was stirred at 70˚C for 72 h. After the completion of the reaction triethylamine (2.9 ml) was added to mixture to quench the catalyst and the flask was cooled down to room temperature with stirring for 1 hour. The polymer was precipitated into water, isolated by filtration, redissolved in tetrahydrofuran (THF) and precipitated into the excess of diethyl ether. The precipitated polymer was isolated by filtration and dried at 80°C/1-2 mbar for 10 h. Yield: 6.63 g (52.4 %). Modification degree (calculated from ^{1}H NMR): 84%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.26 – 6.67 (m, 2H, -NH-), 5.24 – 3.40 (m, 7H), 2.94 (s, 4H), 1.65 – 1.41 (m, 2H), 1.37 (s, 4H), 1.22 (m, 10H), 0.92 – 0.81 (m, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 158.07, 156.49, 155.75, 154.84, 103.38, 100.98, 95.17, 76.74, 74.92, 69.93, 65.78, 62.68, 61.90, 48.48, 40.21, 40.06, 33.54, 31.19, 31.17, 30.01, 29.33, 28.99, 28.60, 28.49, 25.97, 23.56, 23.31, 22.00, 21.94, 17.22, 13.89. T_g (DSC, 10°C/min): 33°C. T_{onset} (TGA, 5°C/min): 215°C. Anal. Calcd. for $C_{17.74}H_{31.84}N_2O_6$: C, 57.72 %; H, 8.69 %; N, 7.59 %; Found: C, 56.29 %; H, 8.14 %; N, 7.36 %.

Example 3

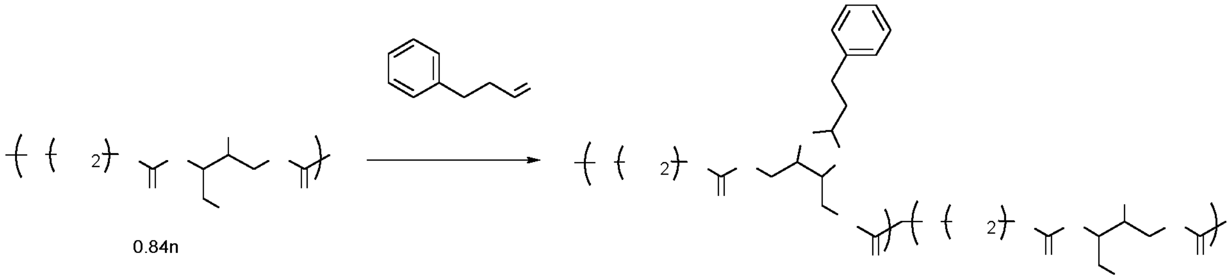
The following synthesis of a modified PHU was performed (Compound C).



The PHU1 polymer (10 g, 34.48 mmol) derived from 1,2:3,4-erythritol dicarbonate (BDC) and hexamethylenediamine (HMDA) was placed in a 250 ml round bottom flask equipped with magnetic stirrer. Then the flask was closed with septum, evacuated, and filled with argon. The 80 ml of anhydrous N-methyl-2-pyrrolidone was added to the flask using syringe and the polymer was dissolved over 1 hour at 70°C with continuous stirring. Then the solution of a catalyst – p-toluenesulfonic acid (p-TSA) (2.489 g, 13.1 mmol) in 5 ml of anhydrous N-methyl-2-pyrrolidone was added and stirred over 5 minutes. Finally, p-trifluoromethylbenzaldehyde (33.8 g, 194.14 mmol) was added via syringe and the reaction mixture was stirred at 70°C for 72 h. After the completion of the reaction triethylamine (3 ml) was added to the mixture to quench the catalyst and the flask was cooled down to room temperature with stirring for 1 hour. The polymer was precipitated into water, isolated by filtration, redissolved in tetrahydrofuran (THF) and precipitated into the excess of diethyl ether. The precipitated polymer was isolated by filtration and dried at 80°C/1-2 mbar for 10 h. Yield: 9.3 g (60.5 %). Modification degree (calculated from ^{19}F NMR with external reference hexafluorobenzene (36.4 mg C_6F_6 and 17.8 mg polymer)): 84%. ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 7.96 – 7.56 (m, 2H), 7.45 – 6.67 (m, 2H), 6.25 – 5.15 (m, 1H), 5.06 – 3.48 (m, 7H), 2.95 (s, 4H), 1.36 (s, 4H), 1.23 (s, 4H). ^{13}C NMR (151 MHz, DMSO-d$_6$) δ 156.51, 155.88, 155.74, 154.87, 141.35, 130.03, 128.40, 128.02, 127.86, 127.33, 127.10, 126.95, 125.18, 123.17, 101.56, 98.98, 77.29, 75.75, 69.94, 67.76, 65.79, 62.52, 61.87, 48.48, 40.77, 40.22, 40.06, 30.10, 30.01, 29.39, 29.34, 29.31, 28.99, 26.00, 25.96, 25.92, 17.22. ^{19}F NMR (565 MHz, DMSO-d$_6$) δ -63.51. T_g (DSC, 10°C/min): 44°C. T_{onset} (TGA, 5°C/min): 195°C. Anal. Calcd. $C_{18.72}H_{24.52}N_2O_6F_{2.52}$: C, 53.35 %; H, 5.86 %; N, 6.65 %; Found: C, 52.56 %; H, 6.0 %; N, 6.66 %.

Example 4

The following synthesis of a modified PHU was performed (Compound D).

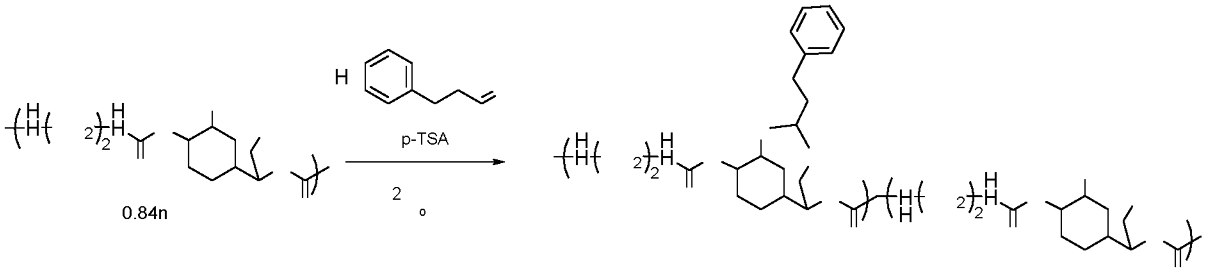


The PHU1 polymer (10 g, 34.48 mmol) derived from 1,2:3,4-erythritol dicarbonate (BDC) and hexamethylenediamine (HMDA) was placed in a 250 ml round bottom flask equipped with magnetic stirrer. Then the flask was closed with septum, evacuated, and filled with argon. The 80 ml of anhydrous N-methyl-2-pyrrolidone was added to the flask using syringe and the polymer was dissolved over 1 hour at

70°C with continuous stirring. Then the solution of a catalyst – p-toluenesulfonic acid (p-TSA) (2.489 g, 13.1 mmol) in 5 ml of anhydrous N-methyl-2-pyrrolidone was added and stirred over 5 minutes. Finally, 3-phenylpropanal (26.05 g, 194.14 mmol) was added via syringe and the reaction mixture was stirred at 70°C for 72 h. After the completion of the reaction triethylamine (3 ml) was added to the mixture to quench the catalyst and the flask was cooled down to room temperature with stirring for 1 hour. The polymer was precipitated into water, isolated by filtration, redissolved in tetrahydrofuran (THF) and precipitated into the excess of diethyl ether. The precipitated polymer was isolated by filtration and dried at 80°C/1-2 mbar for 10 h. Yield: 5.42 g (38.7 %). Modification degree (calculated from ^{1}H NMR): 80%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.44 – 6.64 (m, 7H), 5.28 – 3.35 (m, 7H), 2.93 (s, 4H), 2.63 (q, J = 8.9 Hz, 2H), 1.92 – 1.68 (m, 2H), 1.35 (s, 4H), 1.20 (s, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 156.48, 155.76, 154.86, 141.31, 141.21, 128.29, 128.21, 128.18, 128.14, 125.78, 102.68, 100.27, 76.90, 75.07, 69.93, 67.37, 65.78, 62.65, 61.88, 40.43, 40.22, 40.06, 35.36, 35.13, 30.67, 29.62, 29.31, 29.26, 25.96, 25.93. T_g (DSC, 10°C/min): 46°C. T_{onset} (TGA, 5°C/min): 225°C. Anal. Calcd. $C_{19.2}H_{28.4}N_2O_6$: C, 60.17 %; H, 7.47 %; N, 7.31 %; Found: C, 61.26 %; H, 7.25 %; N, 6.97 %.

Example 5

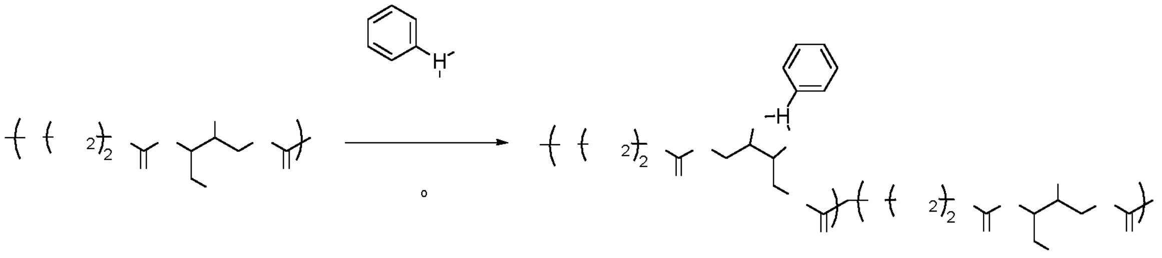
The following synthesis of a modified PHU was performed (Compound E).



The PHU2 polymer (7.9 g, 22.94 mmol) derived from 4-vinylcyclohexene dicarbonate (VCHBC) and hexamethylenediamine (HMDA) was placed in a 250 ml round bottom flask equipped with magnetic stirrer. Then the flask was closed with septum, evacuated, and filled with argon. The 60 ml of anhydrous N-methyl-2-pyrrolidone was added to the flask using syringe and the polymer was dissolved over 1 hour at 70°C with continuous stirring. Then the solution of a catalyst – p-toluenesulfonic acid (p-TSA) (1.656 g, 8.71 mmol) in 5 ml of anhydrous N-methyl-2-pyrrolidone was added and stirred over 5 minutes. Finally, 3-phenylpropanal (17.33 g, 129.14 mmol) was added via syringe and the reaction mixture was stirred at 70 °C for 72 h. After the completion of the reaction triethylamine (3 ml) was added to reaction mixture to quench the catalyst and the flask was cooled down to room temperature with stirring for 1 hour. The polymer was precipitated into water, isolated by filtration, redissolved in tetrahydrofuran (THF) and precipitated into the excess of diethyl ether. The precipitated polymer was isolated by filtration and dried at 80°C/1-2 mbar for 10 h. Yield: 7.45 g (72.1 %). Modification degree (calculated from ^{1}H NMR): 54%. T_g (DSC, 10°C/min): 54°C. T_{onset} (TGA, 5°C/min): 145°C. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.38 – 7.12 (m, 5H), 7.08 – 6.57 (m, 2H), 4.94 – 3.37 (m, 9H), 2.94 (s, 4H), 2.79 – 2.54 (m, 2H), 2.07 – 1.42 (m, 7H), 1.36 (s, 4H), 1.23 (s, 4H), 1.18 – 1.00 (m, 1H).

Example 6

The following synthesis of a modified PHU was performed (Compound F).



The PHU1 polymer (1.5 g, 5.172 mmol) derived from 1,2:3,4-erythritol dicarbonate (BDC) and hexamethylenediamine (HMDA) was placed in a 25 ml round bottom flask equipped with magnetic stirrer. Then the flask was closed with septum, evacuated, and filled with argon. The 18 ml of anhydrous N-methyl-2-pyrrolidone was added to the flask using syringe and the polymer was dissolved over 1 hour at 70°C with continuous stirring. Then, the solution of phenylboronic acid (3.55 g, 29.12 mmol) in 10 ml of anhydrous N-methyl-2-pyrrolidone was added to the reaction mixture and the resulting solution was stirred at 70°C for 72 h. After completion of the reaction, it was cooled down to room temperature with stirring for 1h. The polymer was precipitated into the excess of diethyl ether, isolated by filtration and dried in vacuum at 85°C/1-2 mbar for 10h. Yield: 1.59 g (89.4 %). Modification degree (calculated from ^{1}H NMR): 95%. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.53 –

7.42 (m, 1H), 7.36 – 7.30 (m, 2H), 7.30 – 6.74 (m, 2H), 5.79 – 3.47 (m, 7H), 2.92 (s, 4H), 1.33 (s, 4H), 1.18 (s, 4H).

The following Tables 1 & 2 are depicting the characteristics of the compounds from Examples 1-5.

Table 1. Properties of modified PHU1 and control PHU1 and PU samples.

Polymer	Mod. degree, %	T_g, °C[a]	T_α, °C[b]	E', MPa[c]	T_{onset}, °C[d]	E', Pa[e]			Contact angle (25°C)
						45%	65%	85%	
PU control	-	166[f]	46	1550	200	$4.6\cdot10^{8}$	$4.0\cdot10^{8}$	$3.05\cdot10^{8}$	-
PHU1 control	-	49	56	2100	185	$1.7\cdot10^{9}$	$3.5\cdot10^{8}$	$5.4\cdot10^{7}$	80.3°±0.6°
Compound A	83	35	58	1100	185	$2.1\cdot10^{8}$	$5.3\cdot10^{7}$	$2.7\cdot10^{6}$	106.7°±1.3°
Compound B	82	33	33	1750	215	$8.9\cdot10^{7}$	$2.4\cdot10^{7}$	$2.4\cdot10^{6}$	109.3°±0.5°
Compound C	84	44	-	-	195	$5.3\cdot10^{8}$	$3.3\cdot10^{8}$	$2.0\cdot10^{8}$	84.2°±0.3°
Compound D	80	46	65	1450	225	$4.3\cdot10^{8}$	$3.4\cdot10^{8}$	$7.4\cdot10^{7}$	84.2°±0.9°

[a] Measured using DSC at heating rate of 10°C/min, [b] measured using DMTA, [c] storage modulus measured using DMTA, [d] measured using TGA at heating rate of 5°C/min, [e] storage modulus measured at different humidity levels via rheology method, [f] no T_g was observed on DSC plot, T_m is given instead (heating rate of 10 °C/min)

Table 2. Properties of modified PHU2 sample and control PHU2 sample.

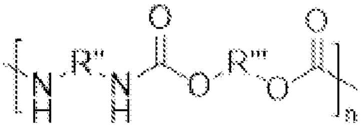
Polymer	Mod. degree, %	T_g, °C[a]	T_{onset}, °C[b]	E', Pa[c]			Contact angle (25 °C)
				45%	65%	85%	
PHU2 control	-	74	195	$5.1\cdot10^{8}$	$2.8\cdot10^{8}$	$7.4\cdot10^{7}$	100.7°±1°
Compound E	54	54	145	$3.7\cdot10^{8}$	$3.6\cdot10^{8}$	$2.3\cdot10^{7}$	106.8°±0.7°

[a] Measured using DSC at heating rate of 10 ˚C/min, [b] measured using TGA at heating rate of 5˚C/min, [c] storage modulus measured at different humidity levels via rheology method

Claims

1. A process for preparing a modified polyhydroxyurethane (PHU) comprising the step of:

reacting a starting non-modified PHU compound, having repeating units, containing two proximate hydroxyl groups separated by 2 to 7 atoms, of formula (I)



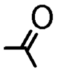
(I)

wherein

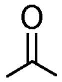
R" is derived from a diamine reagent and is comprised of one or more of the following entities selected from the group consisting of: linear or branched aliphatic, cycloaliphatic and aromatic moeities, oligomeric/(co-)polymeric species, such as poly(alkylene oxides), poly(siloxanes), poly(dienes), poly(olefins), poly(amides), and (co-)polymeric species in the form of amine-terminated oligomers;

R''' is derived from a dicarbonate reagent which consists of terminal carbonate groups, and is comprised of one or more of the following entities selected from the group consisting: linear or branched aliphatic, cycloaliphatic, and aromatic moieties; and additionally, that contains at least 2 hydroxyl functionalities (-OH), said hydroxyl functionalities being separated by no more than 7 atoms;

with a chemical capable of ring formation with the hydroxyl functionalities, selected from the group consisting of an aldehyde compound of formula (II), ketone compound of formula (III) and boronic acid compound of formula (IV)



(II)



(III)

(IV)

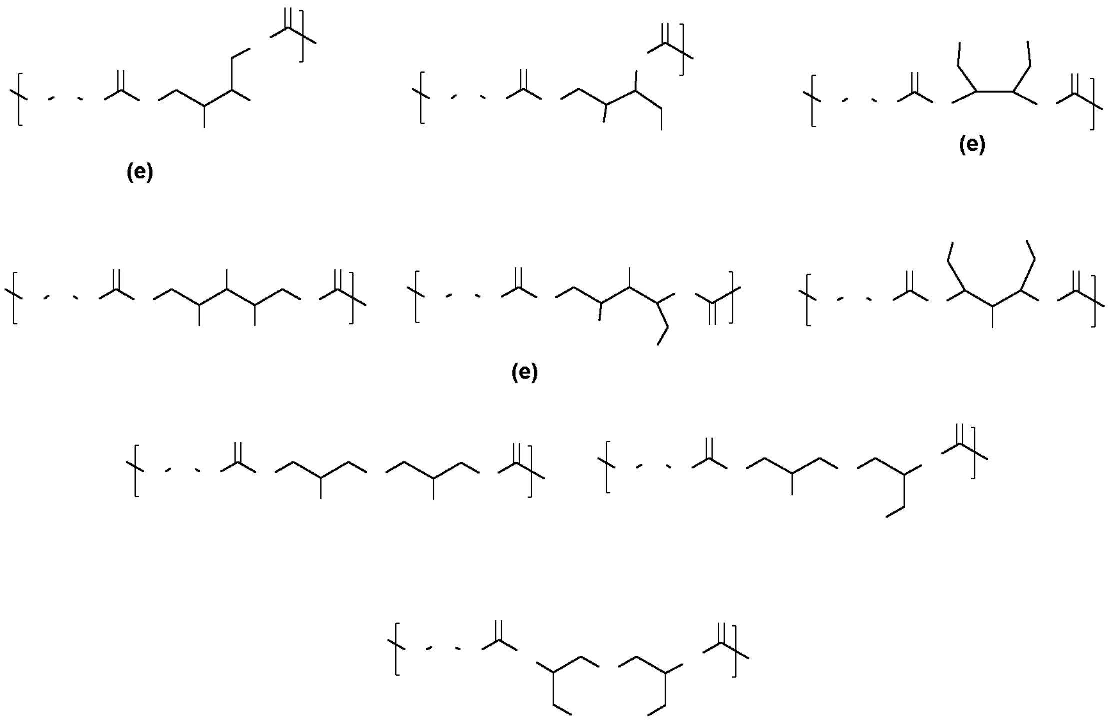
in the presence of a Bronsted acid type catalyst, and a solvent,

at a temperature range of from 40°C to 100°C, during 24h-96h, wherein

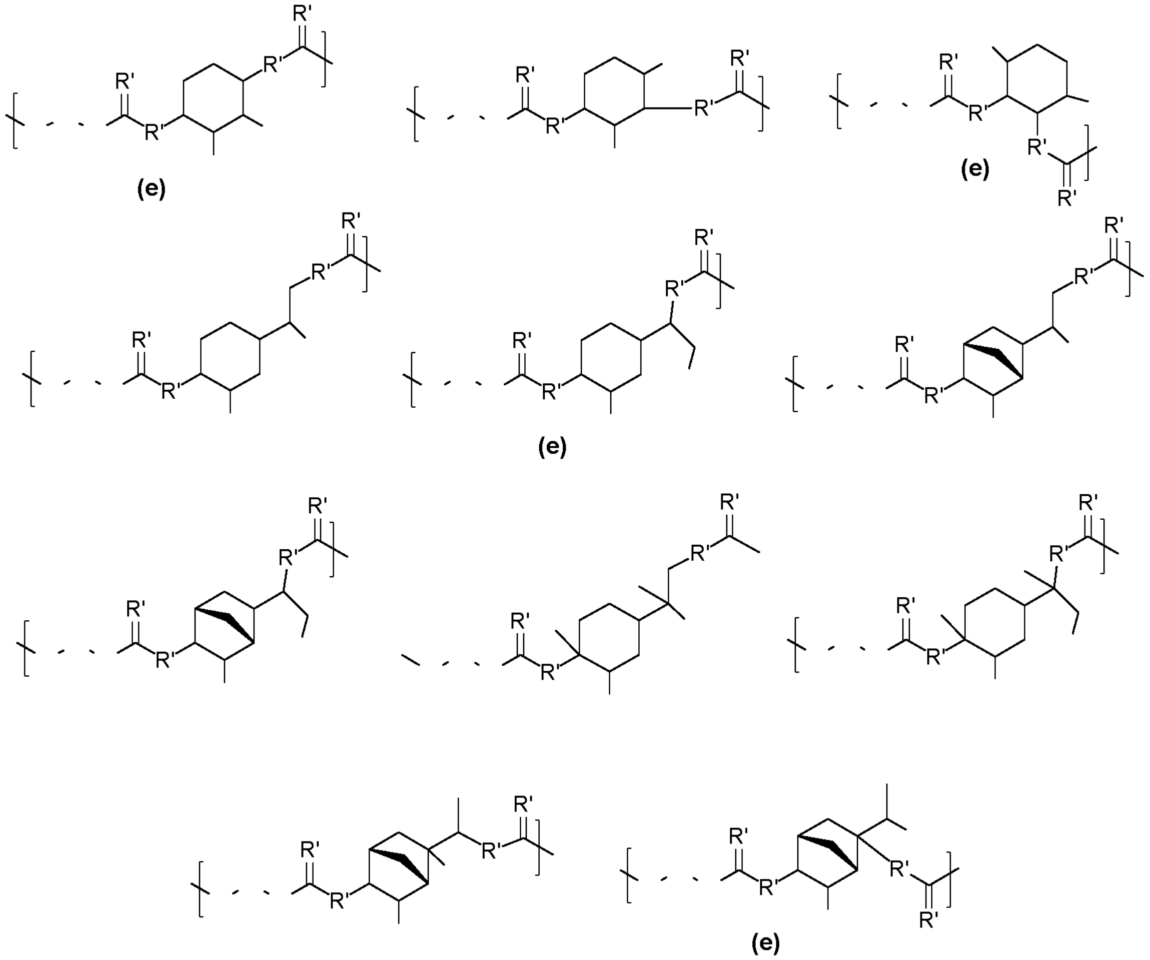
n, is integer of from 5 to 150;

R, R’ are, independently, selected from the group consisting of a linear or branched C_1-C_{10} alkyl or alkoxy group; a linear or branched C_2-C_{10} alkenyl or alkylenoxy group; a linear or branched C_2-C_{10} alkynyl group; a cyclo(C_3-C_6 alkyl) group; a heterocyclo(C_3-C_6 alkyl) group, wherein the hetero atom is selected from N, S, and O; at least one linear or branched C_1-C_6 alkyl group, C_2-C_6 alkenyl or alkylenoxy group, a linear or branched C_2-C_6 alkynyl group, $(CH_2)_m$-Ar group, where Ar is any aromatic ring or condensed aromatic ring, additionally substituted or unsubstituted, optionally including heterocycles, $-(CH_2)_m-CF_3$ group, $-CH_2-(CF_2)_m-CF_3$ group, o-, m-, p- substituted or unsubstituted phenyl group, polycyclic aromatic (PAH), heteroaromatic hydrocarbon and a keto heteroaromatic hydrocarbon, wherein m is of from 0 to 6.

2. The process according to claim 1, wherein the starting non-modified PHU compound of formula (I) is an isomeric linear PHU of formula (Ia) and/or a cycloaliphatic PHU of formula (Ib)



(Ia)



(Ib)

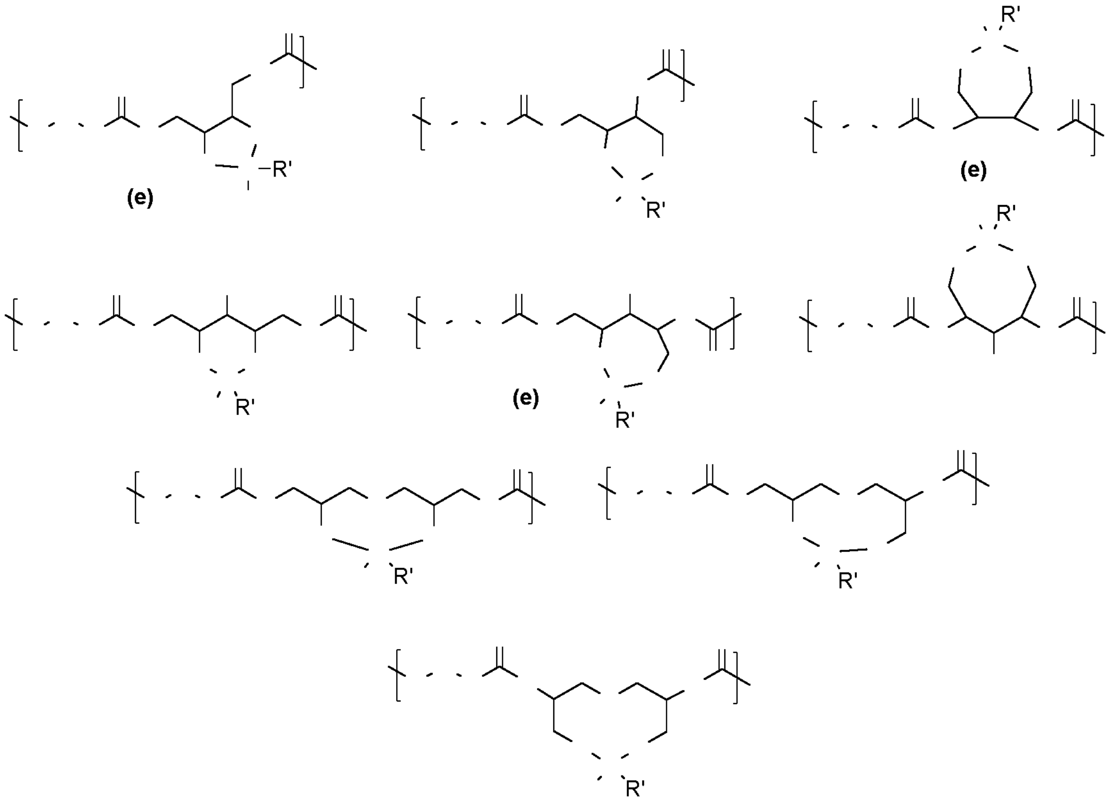
3. The process according to claim 1 or 2, wherein

R and R', independently, are selected from the group consisting of a linear or branched C_1-C_8 alkyl or alkoxy group; a linear or branched C_2-C_8 alkenyl or alkylenoxy group; a linear or branched C_2-C_8 alkynyl group; a cyclo(C_3-C_6alkyl) group; a heteocyclo(C_3-C_6alkyl) group, wherein the hetero atom is selected from N, S, and O; at least one linear or branched C_1-C_6 alkyl group, C_2-C_6 alkenyl or alkylenoxy group, a linear or branched C_2-C_6 alkynyl group; $-(CH_2)_m$-Ar group, where Ar is any aromatic ring or condensed aromatic ring, additionally substituted or unsubstituted, optionally including heterocycles, such as O, N, S; $-(CH_2)_m-CF_3$ group o-, m-, p- substituted or unsubstituted phenyl group, polycyclic aromatic (PAH), heteroaromatic hydrocarbon and a keto heteroaromatic hydrocarbon, wherein m is of from 0 to 4, such as 4-butanal-8-hydroxycumarine and $HOC-(CH_2)_m$-Ar preferably selected form α-tolyaldehyde, cinnamaldehyde and hydrocinnamaldehyde.

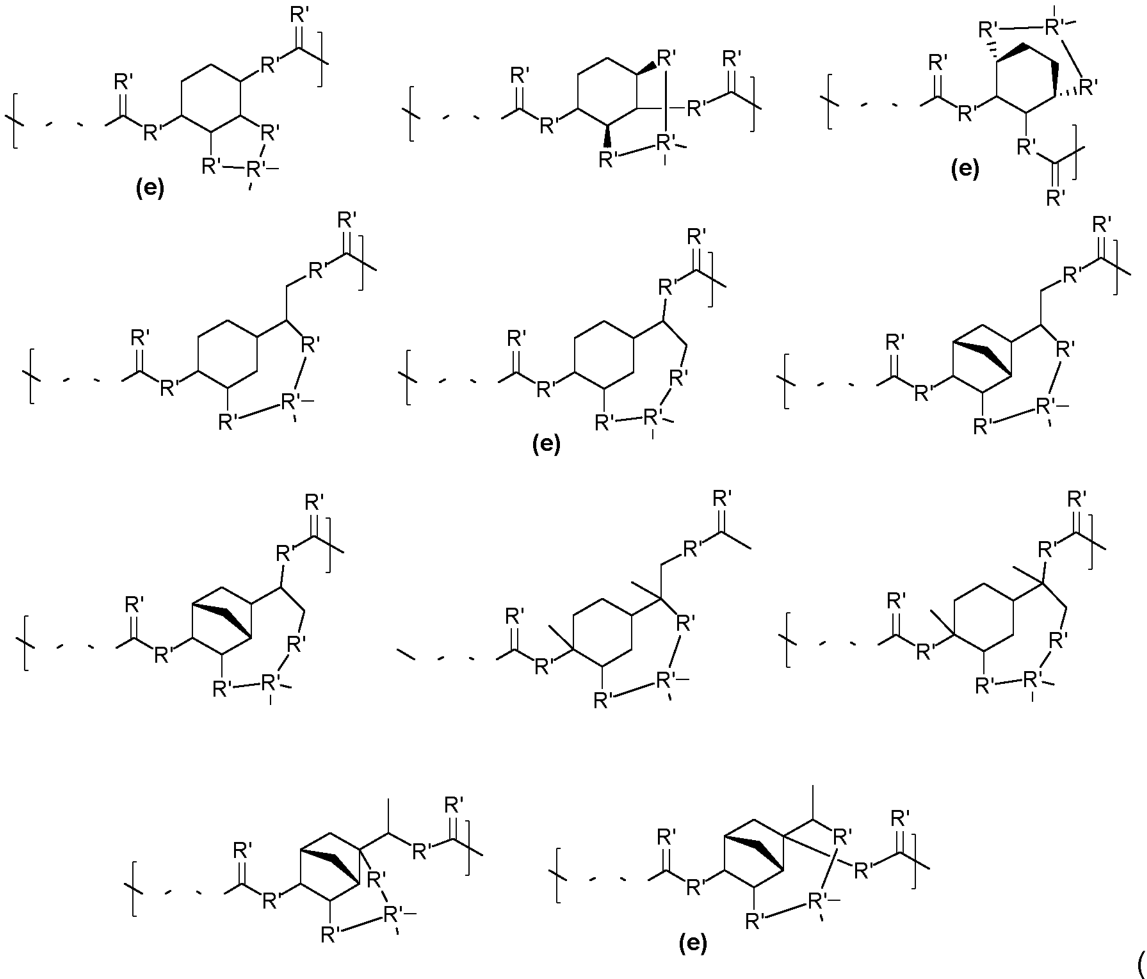
4. The process according to any of claims 1-3, wherein the Bronsted acid type catalyst is selected from p-toluenesulfonic acid (p-TCA), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), acetic acid (CH_3COOH), methanesulfionic acid (CF_3SO_3H), tetrafluoroboric acid (HBF_4) and hexafluorophosphoric acid (HPF_6), and mixtures thereof.

5. The process according to any of claims 1-4, wherein the solvent is selected from n-methyl-2-pyrrolidone (NMP), N,N-Dimethylformamide (DMF), N,N-Dimethylacetamide (DMAC), Dimethyl sulfoxide (DMSO), and mixture thereof, or other polar solvent capable to dissolve the starting non modified PHU(s).

6. Modified poly(hydroxyurethanes) (PHUs) obtainable by the process of any of claims 1-5 presenting an isomeric linear structure of formula (V) and/or a cycloaliphatic structure of formula (VI) selected from the group consisting of



(V)



(VI)

wherein R, R’, R” and n have the same meanings as defined in any of claims 1-5.

7. The modified poly(hydroxyurethanes) according to claim 6, wherein said modified poly(hydroxyurethanes) is aldehyde modified PHUs, ketone modified PHUs and boronic acid modified PHUs.

8. The modified poly(hydroxyurethanes) according to claim 6 or 7, wherein the modified PHU(s) are exhibiting a water adsorption, in wt. %, which is reduced of at least 70% as compared to the starting non modified PHU(s), said water adsorption being measured according to with ASTM E337-15 standard, preferably the water adsorption being reduced from 1,7 to 10 fold with comparison to the starting non modified PHU(s), at same experimental conditions.

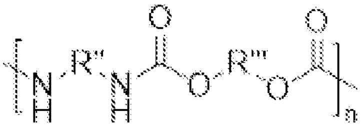
9. The modified poly(hydroxyurethanes) according to any of claims 6 to 8, wherein the modified PHU(s) exhibit a contact angle increase of about 5-36% in comparison with the starting non modified PHU(s), at same experimental conditions.

10. The modified poly(hydroxyurethanes) according to any of claims 6 to 9, wherein the modified poly(hydroxyurethanes) (PHUs) exhibit modification degrees in the range of 75-95%, preferably of from 80 to 85%, in comparison to a starting non-modified PHU compound.

Revendications

1. Procédé de préparation d'un polyhydroxyuréthane (PHU) modifié comprenant les étapes suivantes consistant à :

faire réagir un composé PHU non modifié de départ, ayant des motifs répétitifs, contenant deux groupes hydroxyle proximaux séparés par 2 à 7 atomes, de formule (I)



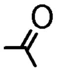
(I)

dans laquelle

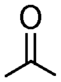
R'' est dérivé d'un réactif diamine, et est constitué d'une ou plusieurs des entités suivantes choisies dans le groupe constitué par : des parties aliphatiques linéaires ou ramifiées, cycloaliphatiques et aromatiques, les espèces oligomères/(co-)polymères, telles que les poly(oxydes d'alkylène), les poly(siloxanes), les poly(diènes), les poly(oléfines), les poly(amides), et les espèces (co-)polymères sous la forme d'oligomères à terminaison amine ;

R''' est dérivé d'un réactif dicarbonate qui consiste en des groupes carbonate terminaux, et est constitué d'une ou plusieurs des entités suivantes choisies dans le groupe constitué par : des parties aliphatiques linéaires ou ramifiées, cycloaliphatiques et aromatiques ; et, en outre, qui contient au moins 2 fonctionnalités hydroxyle (-OH), lesdites fonctionnalités hydroxyle étant séparées par pas plus de 7 atomes ;

avec un produit chimique capable de former un cycle avec les fonctionnalités hydroxyle, choisi dans le groupe constitué par un composé aldéhyde de formule (II), un composé cétonique de formule (III) et un composé acide boronique de formule (IV)



(II)



(III)

(IV)

en présence d'un catalyseur de type acide de Bronsted, et d'un solvant,

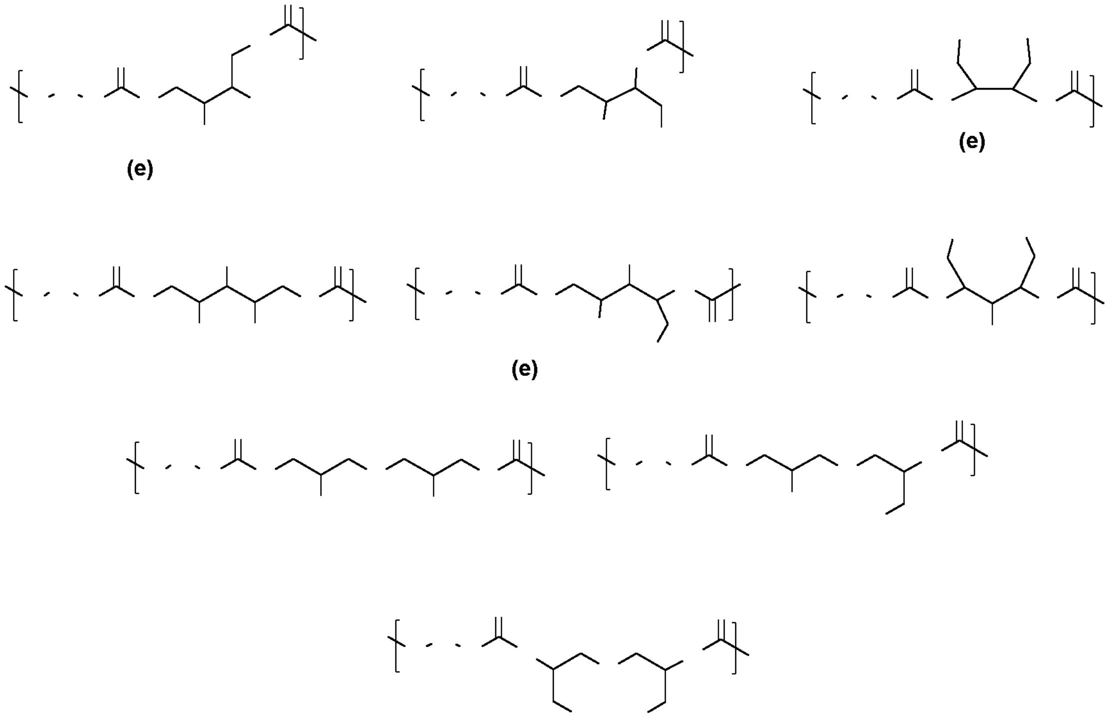
à une température comprise entre 40°C et 100°C, pendant 24 à 96 heures,

dans laquelle

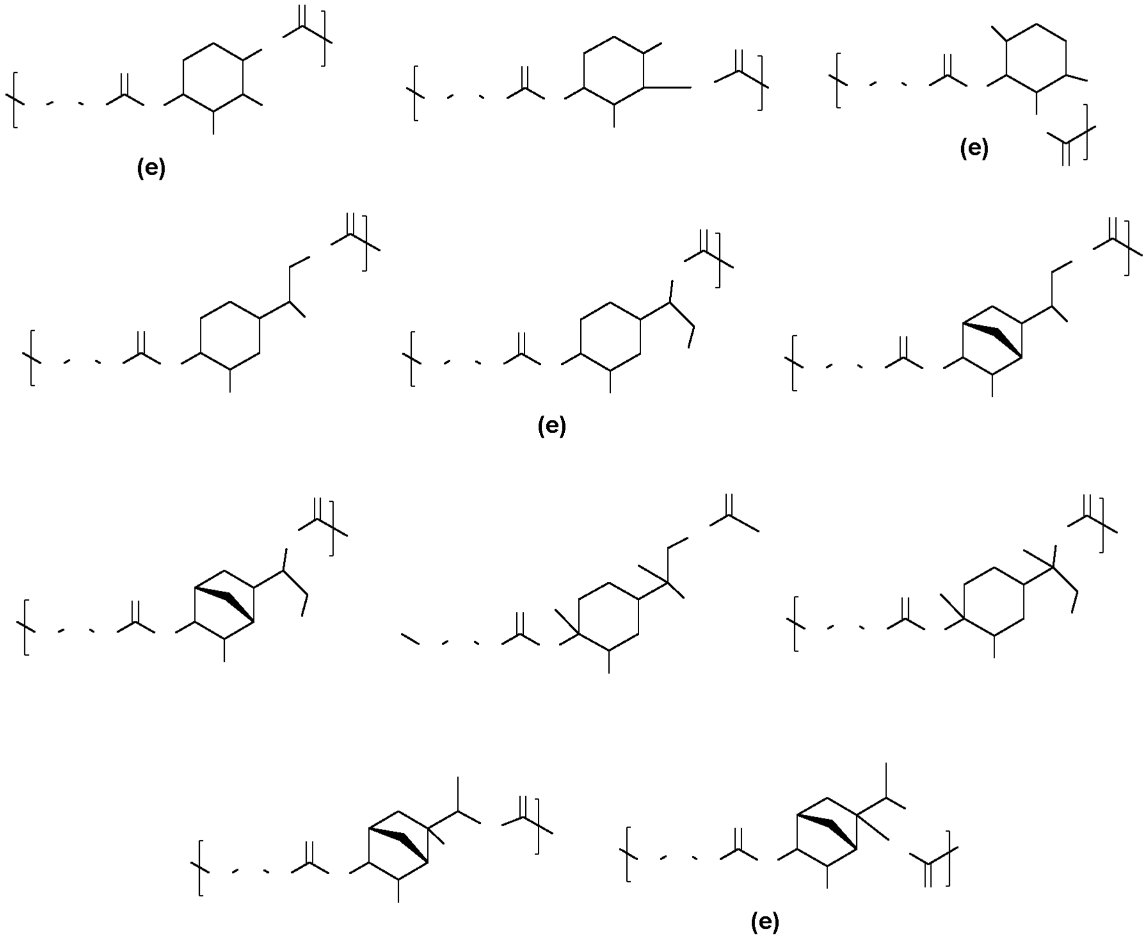
- n est un nombre entier de 5 à 150 ;

- R, R' sont, indépendamment, choisis dans le groupe constitué par un groupe alkyle ou alcoxy en C_1-C_{10} linéaire ou ramifié ; un groupe alcényle ou alkylénoxy en C_2-C_{10} linéaire ou ramifié ; un groupe alcynyle en C_2-C_{10} linéaire ou ramifié ; un groupe cyclo(alkyle en C_3-C_6) ; un groupe hétérocyclo(alkyle en C_3-C_6), dans lequel l'hétéroatome est choisi parmi N, S et O ; au moins un groupe alkyle en C_1-C_6, un groupe alcényle ou alkylénoxy en C_2-C_6 linéaire ou ramifié, un groupe alcynyle en C_2-C_6 linéaire ou ramifié, un groupe $(CH_2)_m$-Ar, où Ar est tout cycle aromatique ou tout cycle aromatique condensé, en outre substitué ou non substitué, comprenant éventuellement des hétéroatomes, un groupe $-(CH_2)m-CF_3$, un groupe $-CH_2-(CF_2)_m-CF_3$, un groupe phényle o-, m-, p- substitué ou non substitué, un hydrocarbure aromatique polycyclique (PAH), un hydrocarbure hétéroaromatique et un hydrocarbure céto hétéroaromatique, où m est compris entre 0 et 6.

2. Procédé selon la revendication 1, dans lequel le composé PHU non modifié de départ de formule (I) est un PHU linéaire isomère de formule (Ia) et/ou un PHU cycloaliphatique de formule (Ib)



(Ia)



(Ib)

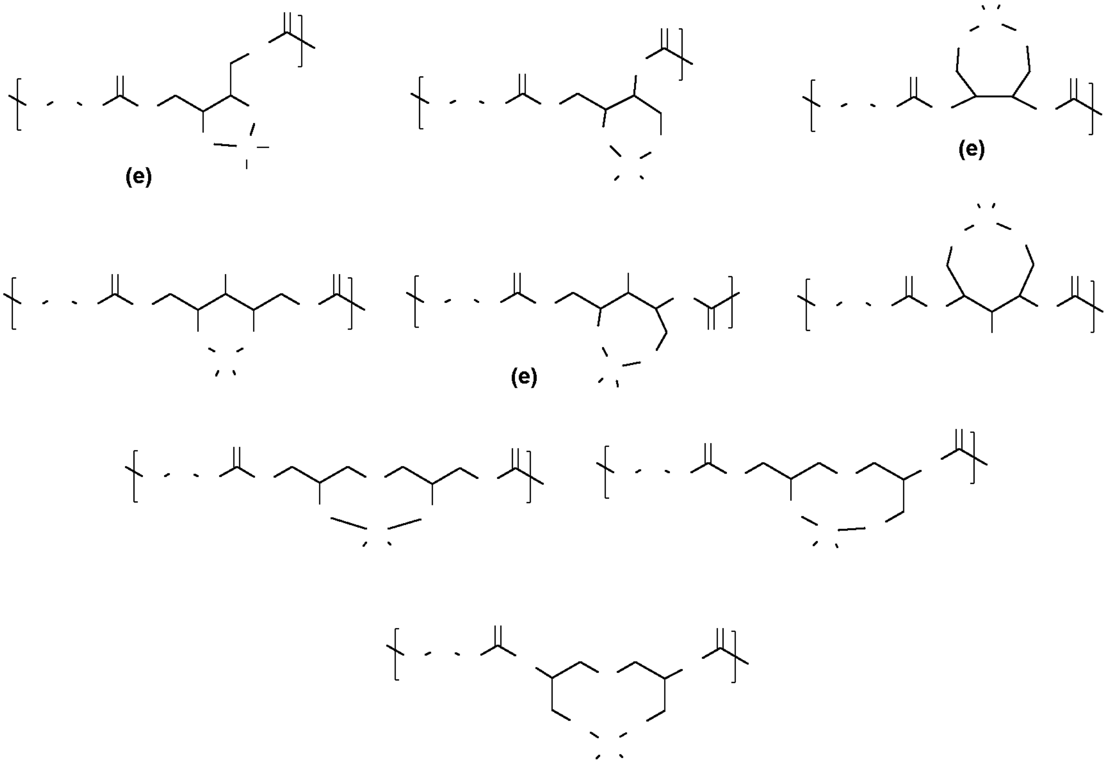
3. Procédé selon la revendication 1 ou 2, dans lequel

R et R', indépendamment, sont choisis dans le groupe constitué par un groupe alkyle ou alcoxy en C_1-C_8 linéaire ou ramifié ; un groupe alcényle ou alkylénoxy en C_2-C_8 linéaire ou ramifié ; un groupe alcynyle en C_2-C_8 linéaire ou ramifié ; un groupe cyclo(alkyle en C_3-C_6) ; un groupe hétérocyclo(alkyle en C_3-C_6), dans lequel l'hétéroatome est choisi parmi N, S et O ; au moins un groupe alkyle en C_1-C_6, un groupe alcényle ou alkylénoxy en C_2-C_6 linéaire ou ramifié, un groupe alcynyle en C_2-C_6 linéaire ou ramifié ; un groupe $-(CH_2)_m-Ar$, où Ar est tout cycle aromatique ou tout cycle aromatique condensé, en outre substitué ou non substitué, comprenant éventuellement des hétéroatomes, tels que O, N, S ; un groupe $-(CH_2)_m-CF_3$, un groupe phényle o-, m-, p- substitué ou non substitué, un groupe aromatique polycyclique (PAH), un hydrocarbure hétéroaromatique et un hydrocarbure céto hétéroaromatique, dans lequel m est compris entre 0 et 4, comme la 4-butanal-8-hydroxycumarine et $HOC-(CH_2)_m-Ar$, de préférence choisi parmi l'α-tolyaldéhyde, le cinnamaldéhyde et l'hydrocinnamaldéhyde.

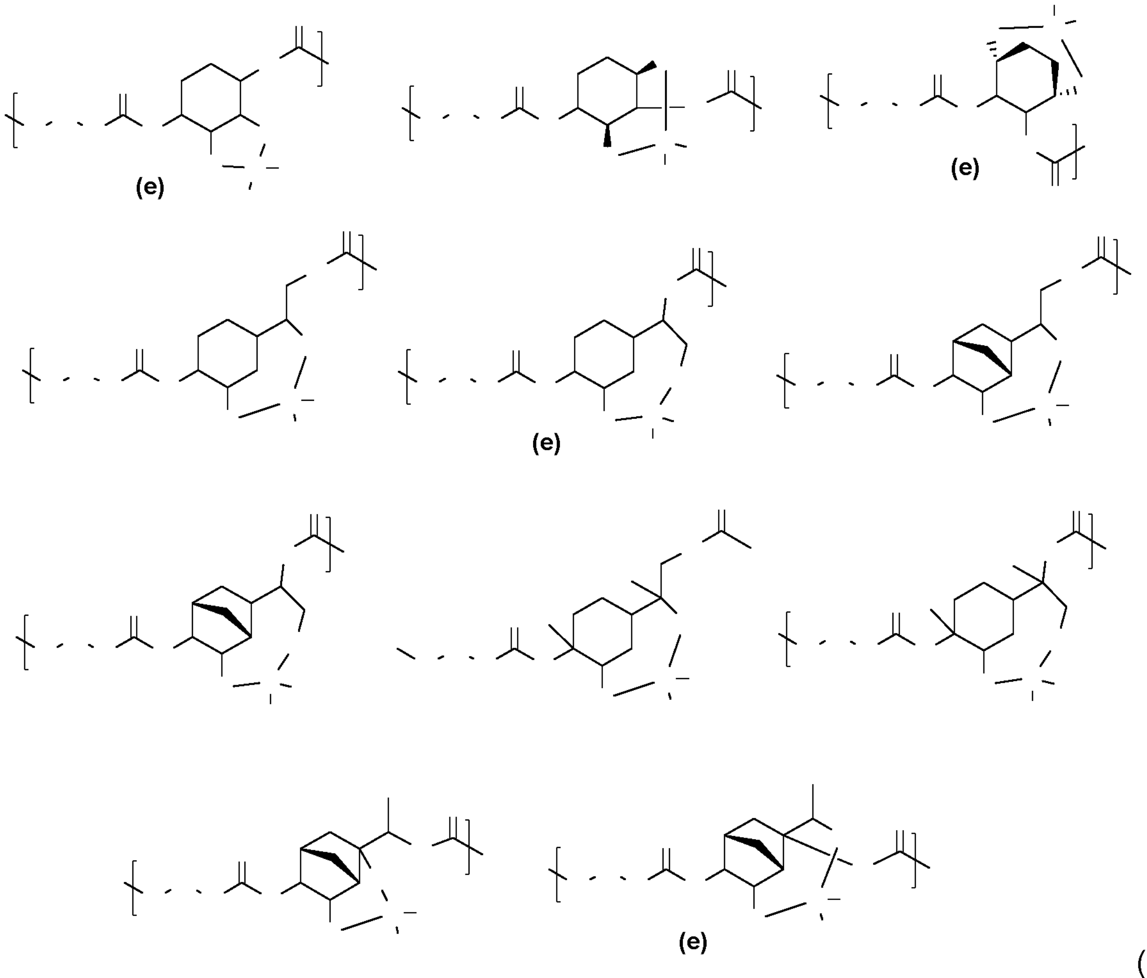
4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le catalyseur de type acide de Bronsted est choisi parmi l'acide p-toluènesulfonique (p-TCA), l'acide chlorhydrique (HCl), l'acide sulfurique (H_2SO_4), l'acide acétique (CH_3COOH), l'acide méthanesulfonique (CF_3SO_3H), l'acide tétrafluoroborique (HBF_4) et l'acide hexafluorophosphorique (HPF_6), et leurs mélanges.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le solvant est choisi parmi la n-méthyl-2-pyrrolidone (NMP), le N,N-diméthylformamide (DMF), le N,N-diméthylacétamide (DMAC), le diméthylsulfoxyde (DMSO), et un mélange de ceux-ci, ou un autre solvant polaire capable de dissoudre le ou les PHU non modifié(s) de départ.

6. Poly(hydroxyuréthanes) (PHU) modifiés pouvant être obtenus par le procédé de l'une quelconque des revendications 1-5, présentant une structure linéaire isomère de formule (V) et/ou une structure cycloaliphatique de formule (VI) choisie dans le groupe constitué par



(V)



(VI)

dans lesquelles R, R', R'' et n ont les mêmes significations que celles définies dans l'une quelconque des revendications 1 à 5.

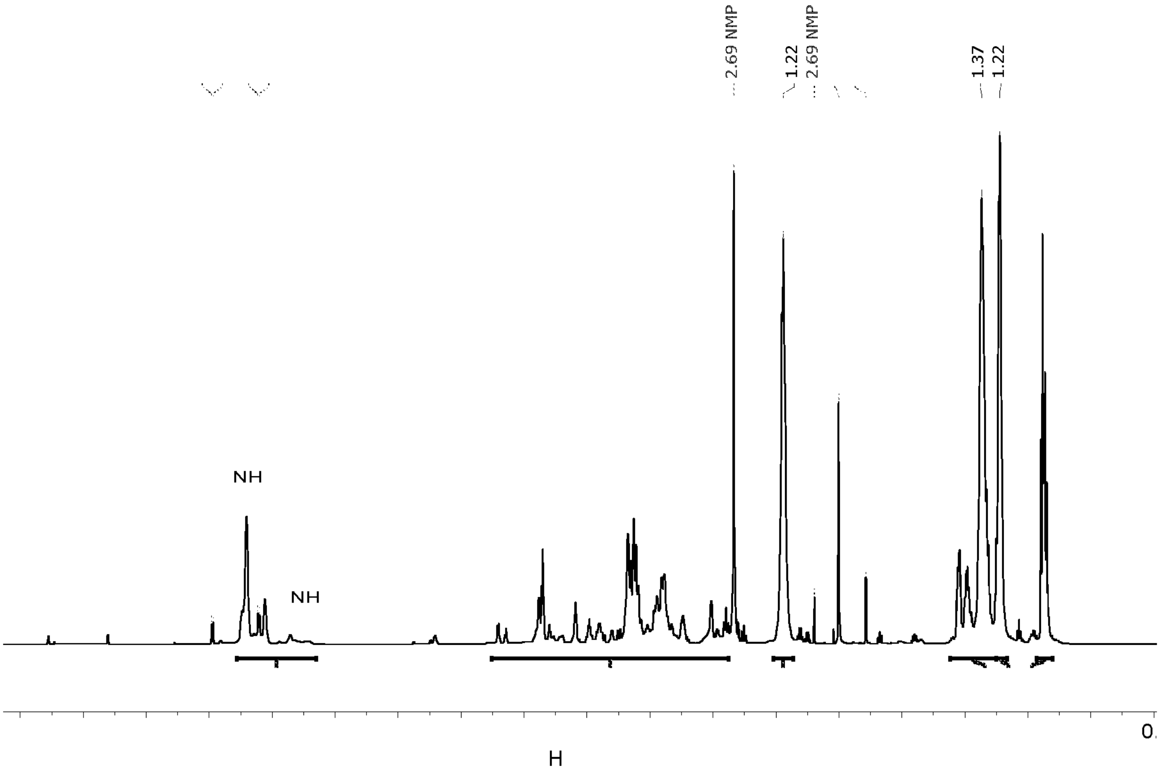
7. Poly(hydroxyuréthanes) modifiés selon la revendication 6, dans lesquels lesdits poly(hydroxyuréthanes) modifiés sont des PHUs modifiés par un aldéhyde, des PHUs modifiés par une cétone et des PHUs modifiés par un acide boronique.

8. Poly(hydroxyuréthanes) modifiés selon la revendication 6 ou 7, dans lesquels le ou les PHU modifié(s) présentent une adsorption d'eau, en % en poids, qui est réduite d'au moins 70 % par rapport au(x) PHU non modifié(s) de départ, ladite adsorption d'eau étant mesurée selon la norme ASTM E337-15, de préférence l'adsorption d'eau étant réduite de 1,7 à 10 fois par rapport au(x) PHU non modifié(s) de départ, dans les mêmes conditions expérimentales.

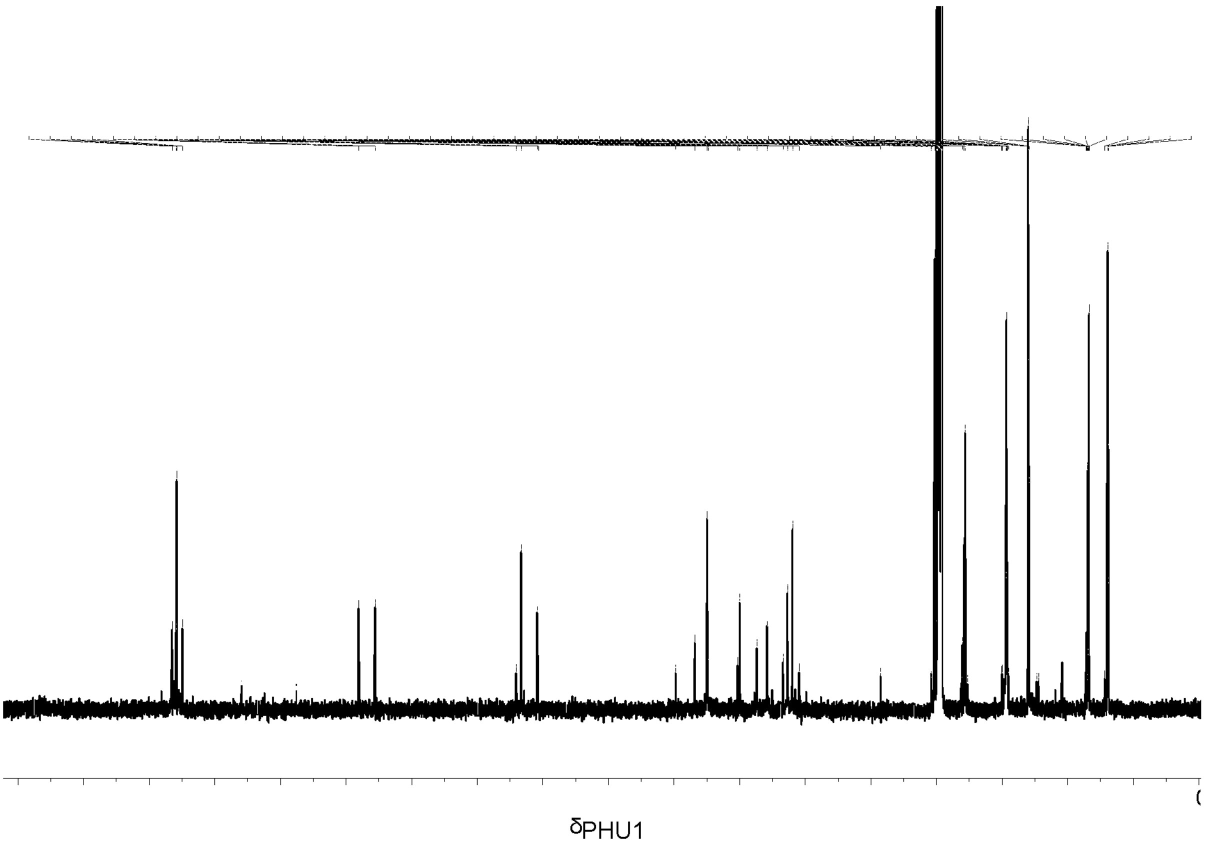
9. Poly(hydroxyuréthanes) modifiés selon l'une quelconque des revendications 6 à 8, dans lesquels le ou les PHU modifié(s) présentent une augmentation de l'angle de contact d'environ 5 à 36% par rapport au(x) PHU non modifié(s) de départ, dans les mêmes conditions expérimentales.

10. Poly(hydroxyuréthanes) modifiés selon l'une quelconque des revendications 6 à 9, dans lesquels les poly(hydroxyuréthanes) (PHU) modifiés présentent des degrés de modification dans la gamme de 75-95%, de préférence de 80 à 85%, par rapport au composé PHU non modifié de départ.

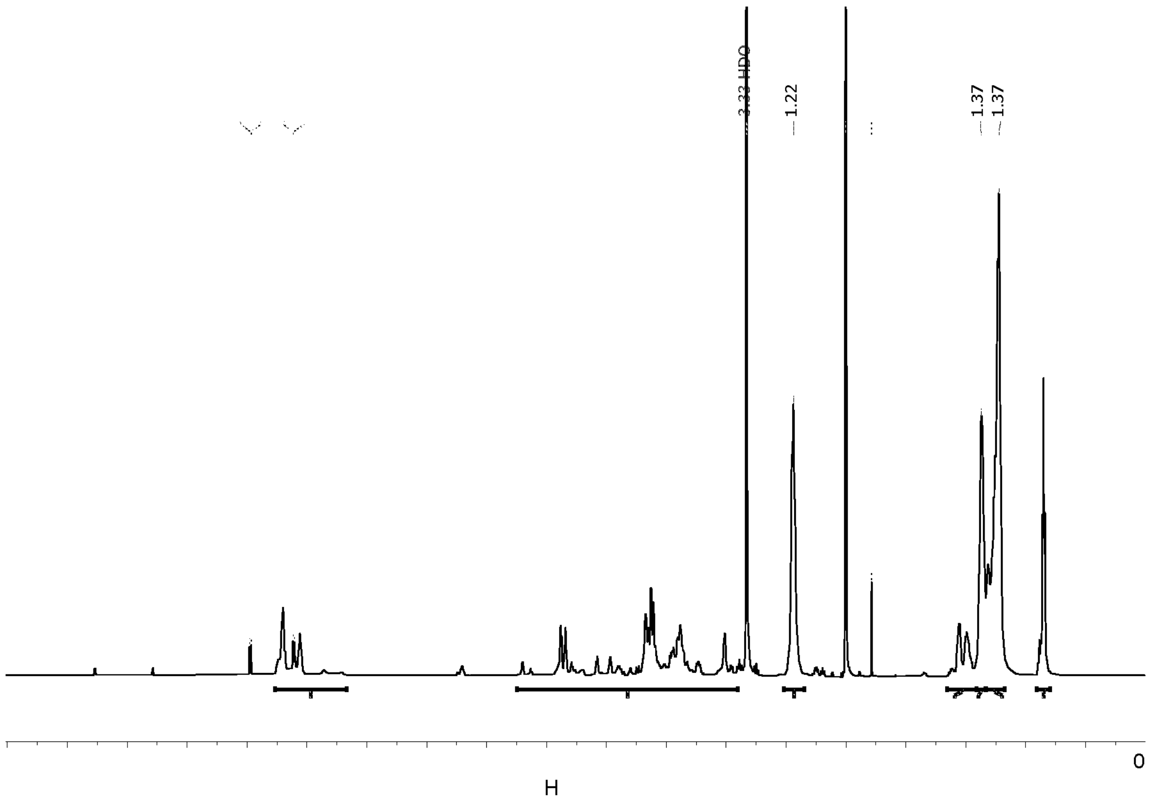
[Fig 1a)]



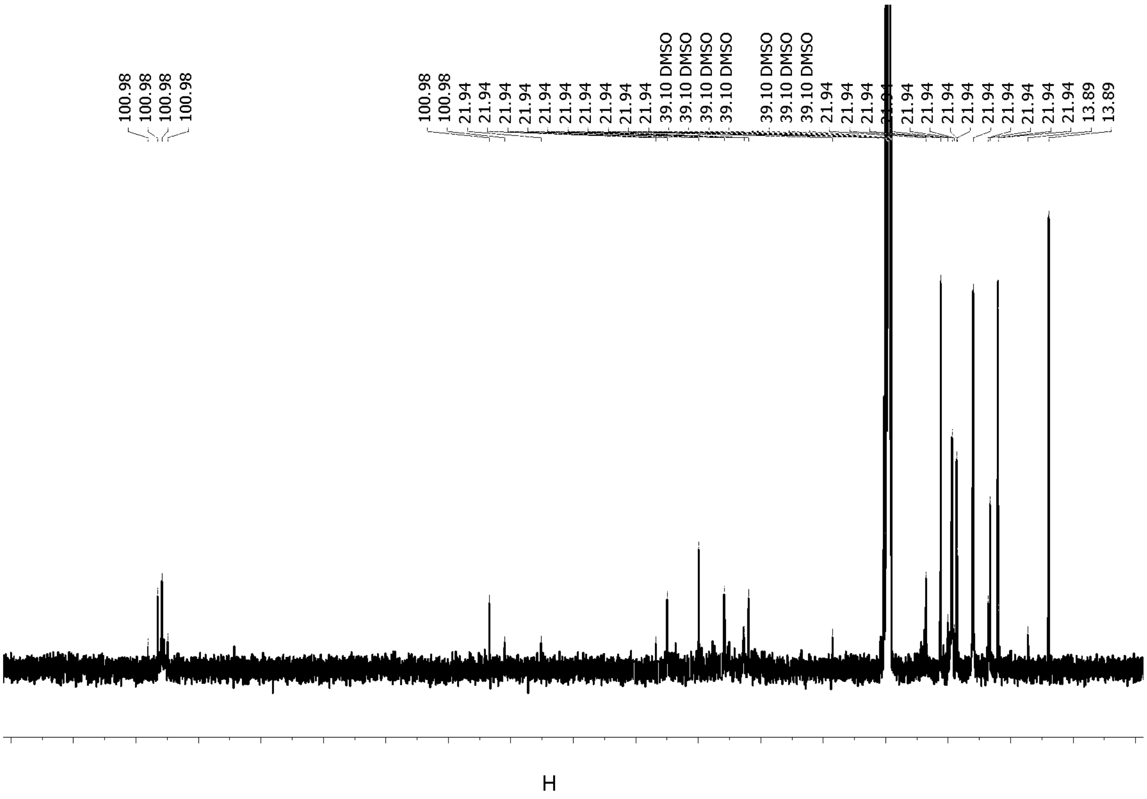
[Fig 1b)]



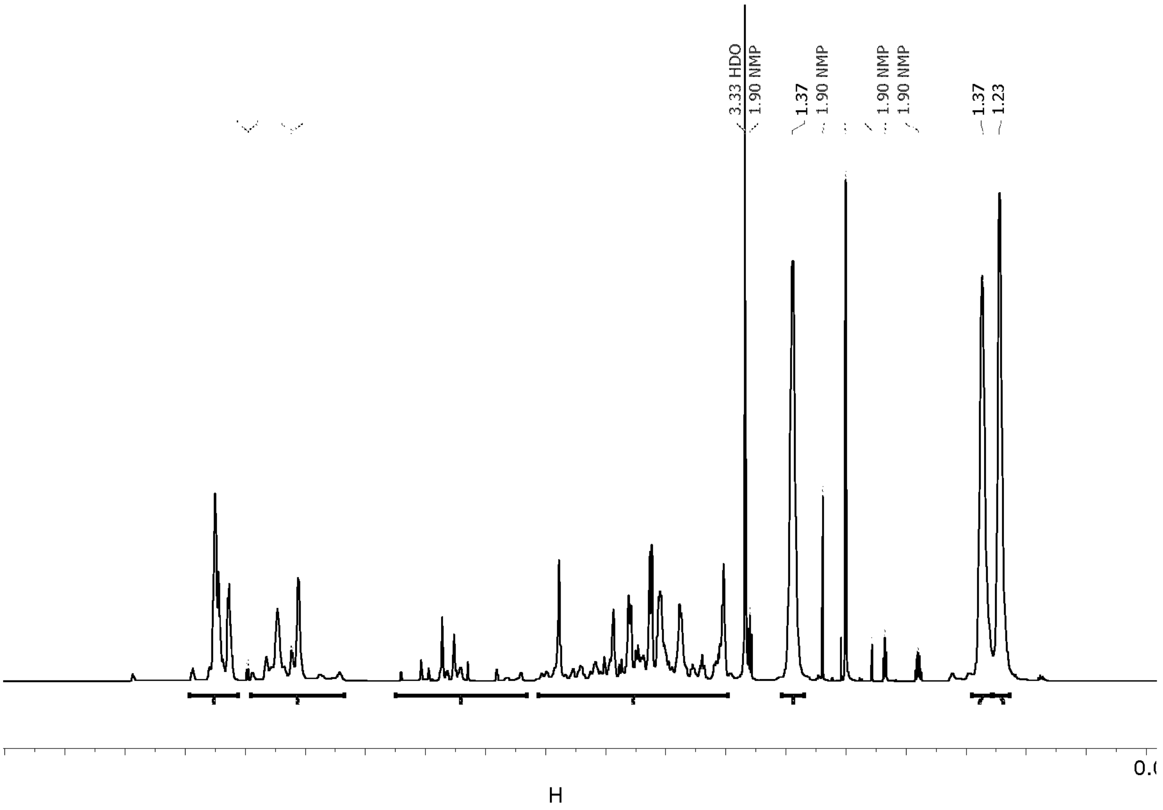
[Fig 2a)]


3.33 HDO
1.22
1.37
1.37
0
H

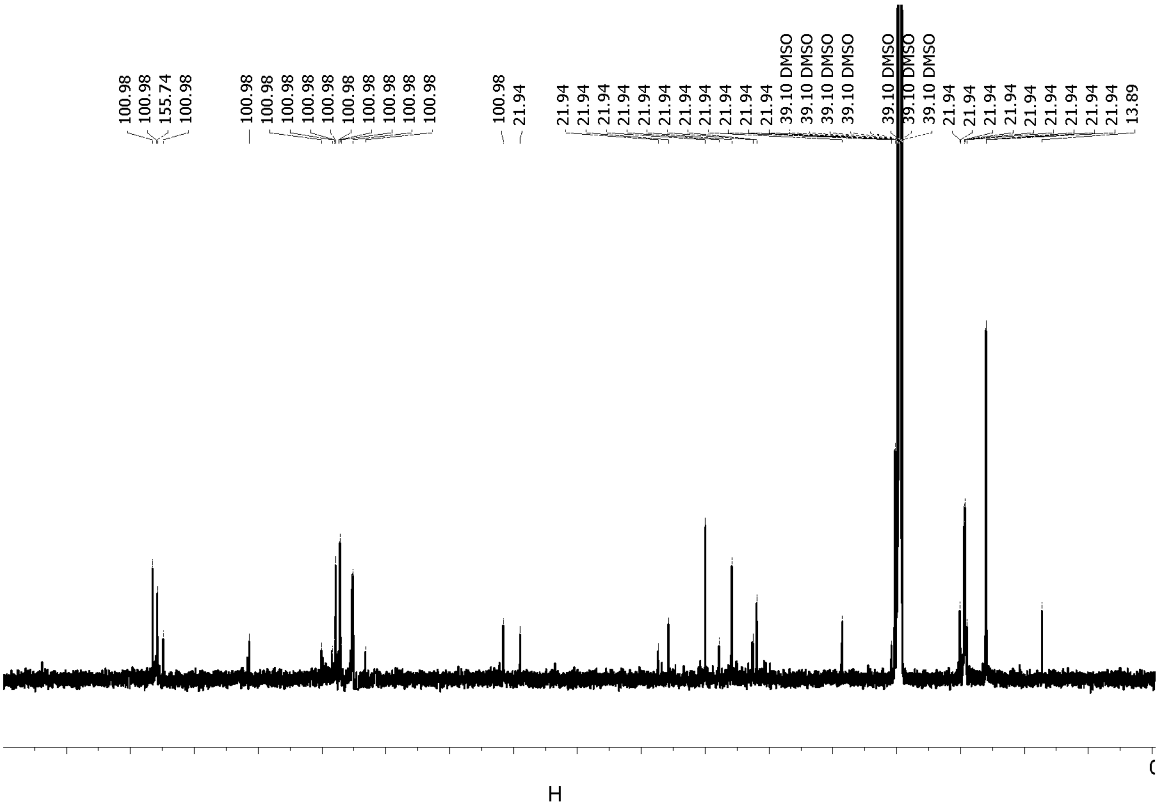
[Fig 2b)]


100.98
100.98
100.98
100.98
100.98
100.98
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
13.89
13.89
H

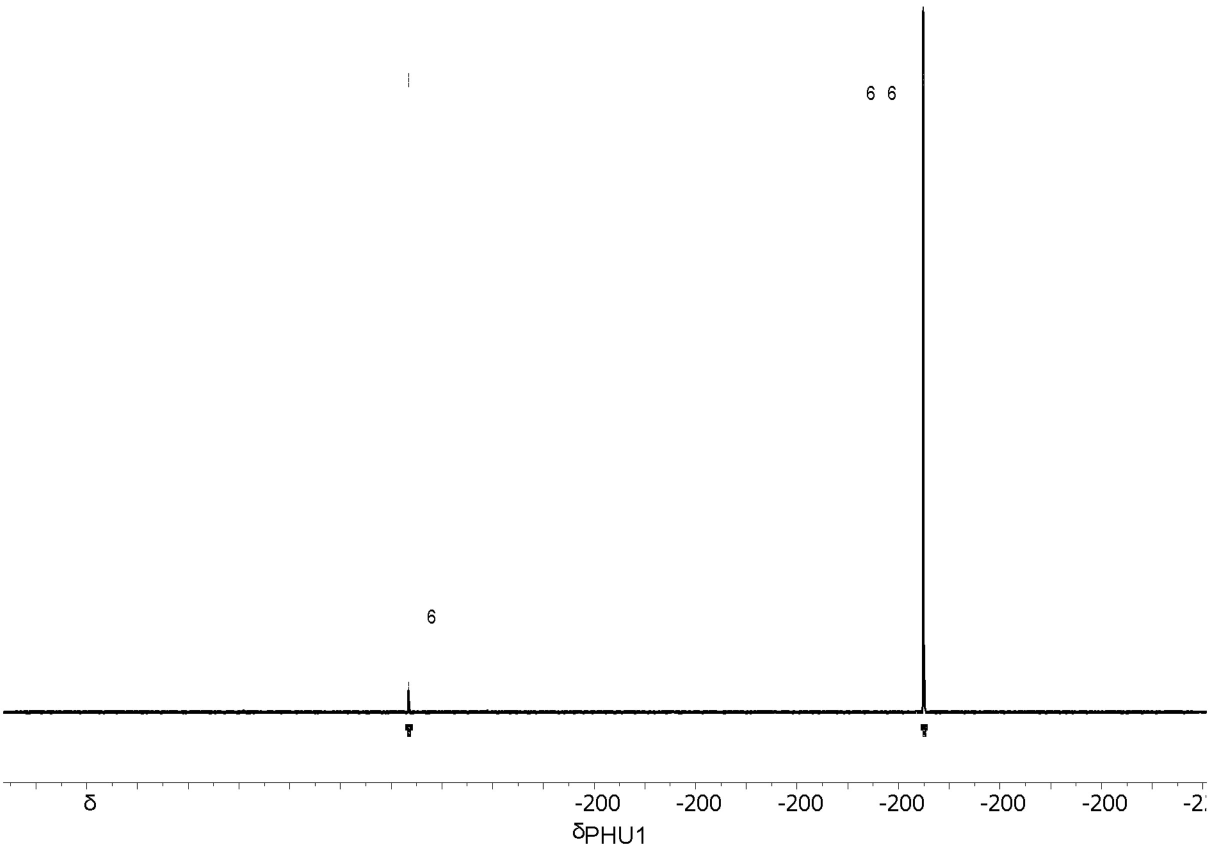
[Fig 3a)]


3.33 HDO
1.90 NMP
1.37
1.90 NMP
1.90 NMP
1.90 NMP
1.37
1.23
0.(
H

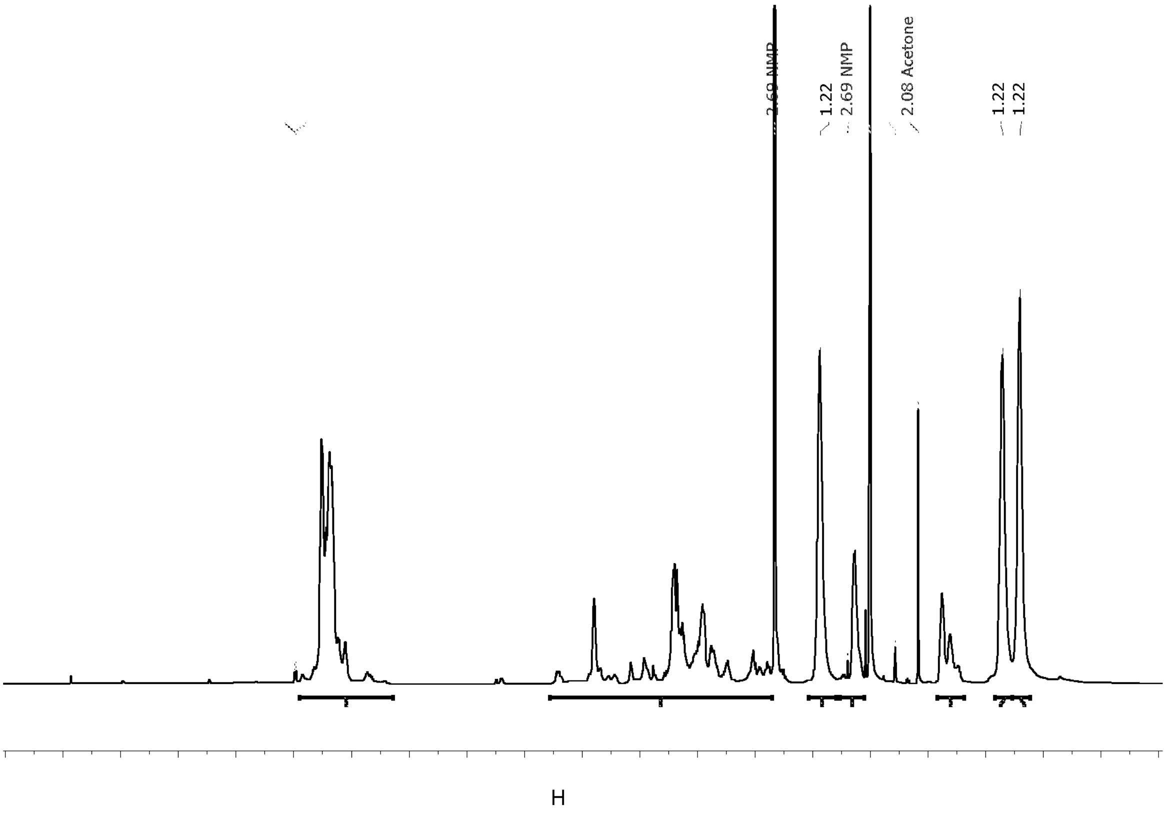
[Fig 3b)]


100.98
100.98
155.74
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
13.89
(
H

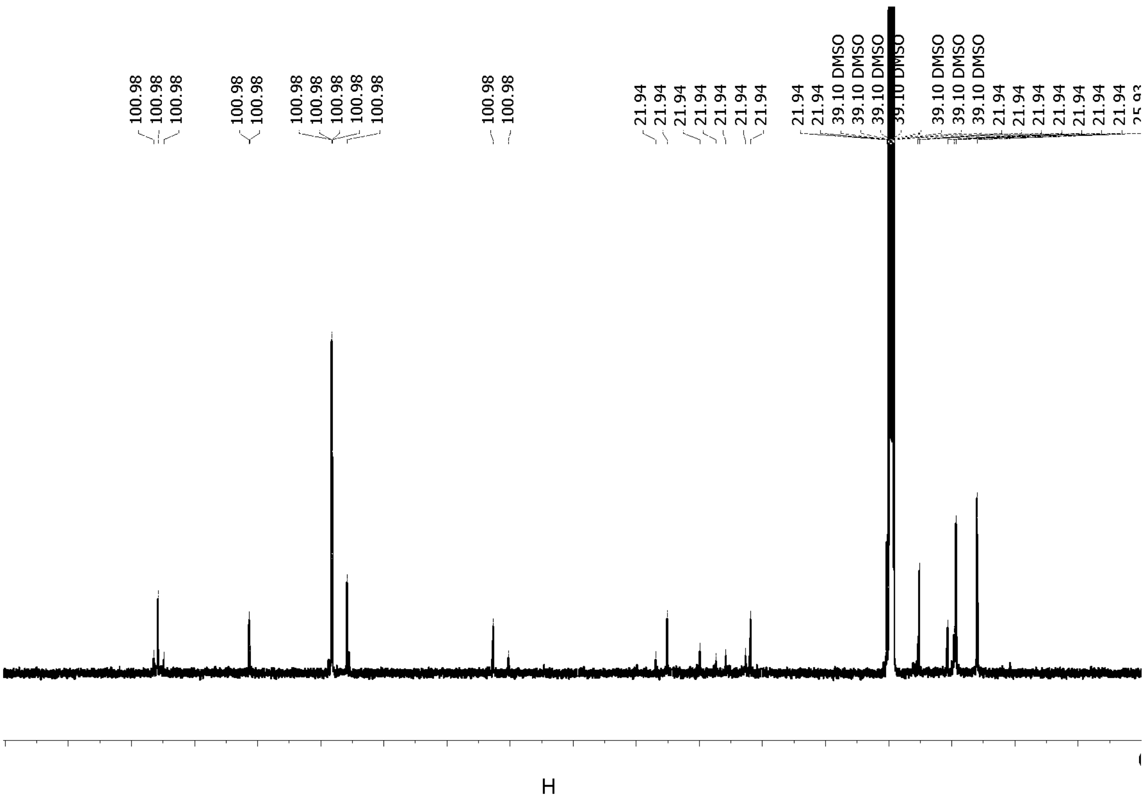
[Fig 3c)]


6 6
6
δ
-200
-200
-200
-200
-200
-200
-2
δPHU1

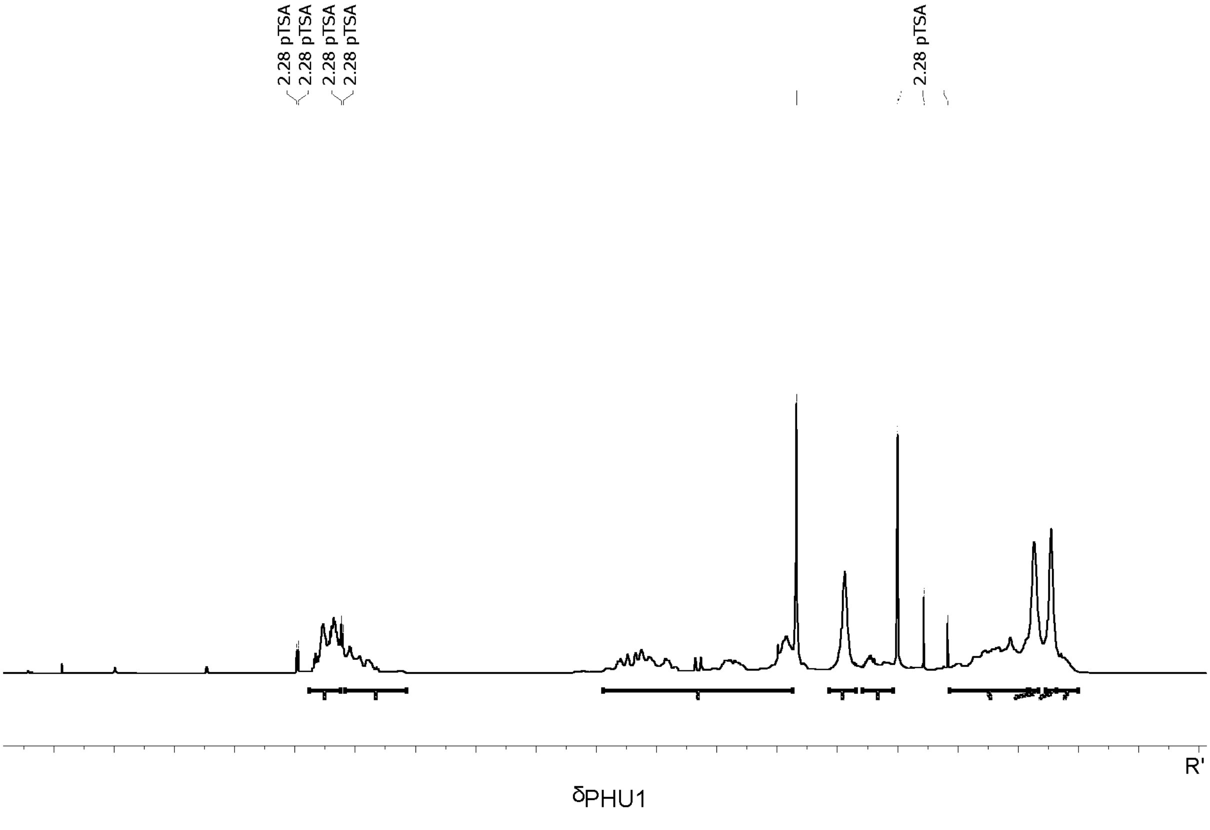
[Fig 4a)]


2.69 NMP
1.22
2.69 NMP
2.08 Acetone
1.22
1.22
H

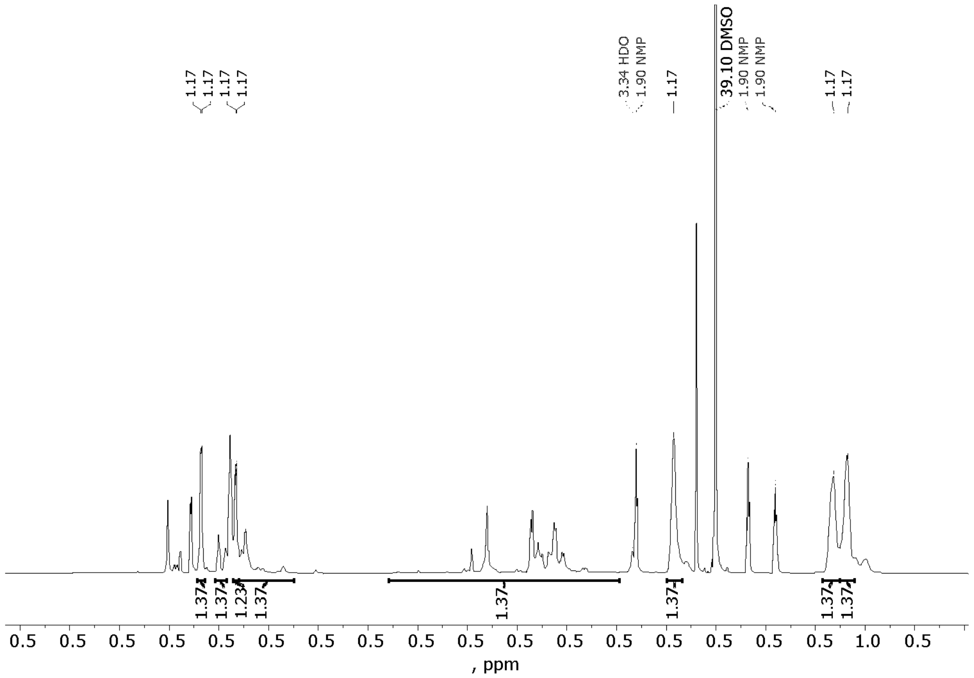
[Fig 4b)]


100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
100.98
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
21.94
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
39.10 DMSO
21.94
21.94
21.94
21.94
21.94
21.94
21.94
H

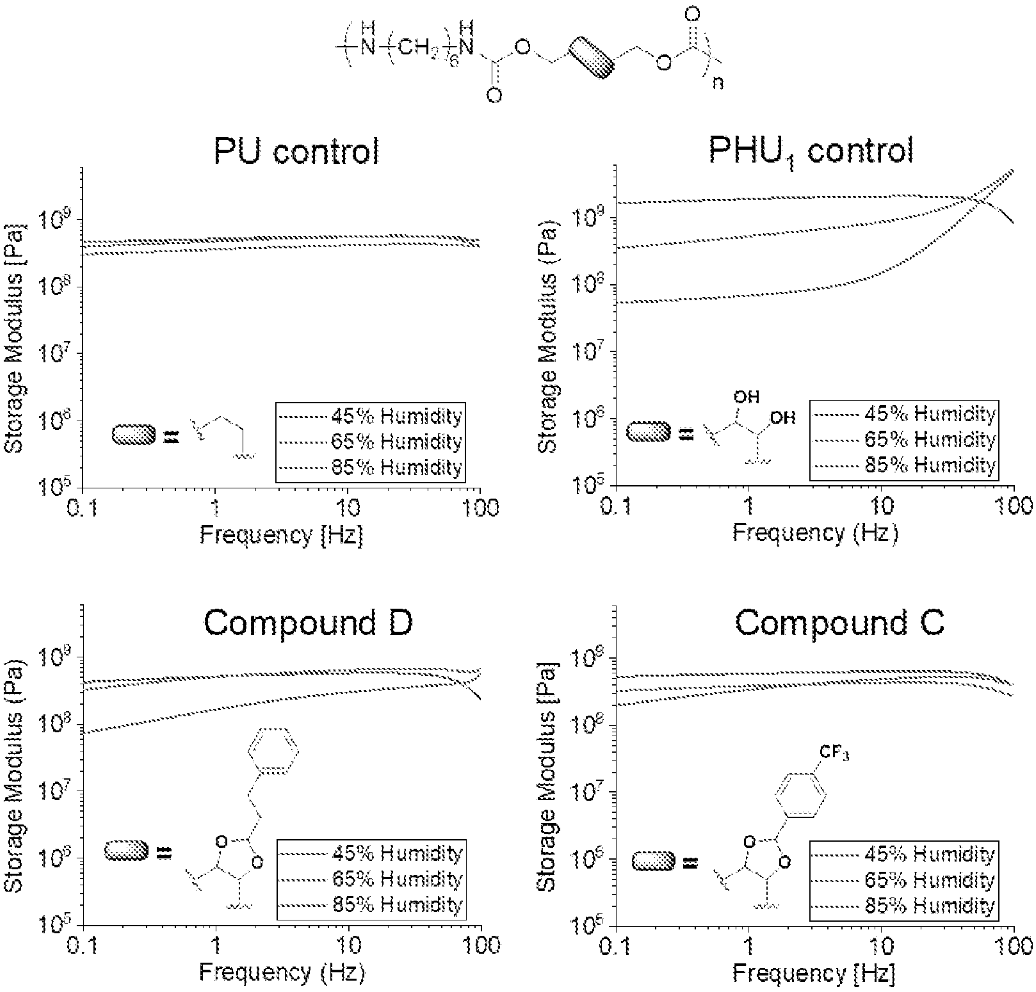
[Fig 5]


2.28 pTSA
2.28 pTSA
2.28 pTSA
2.28 pTSA
2.28 pTSA
R'
δPHU1

[Fig 6]


1.17
1.17
1.17
1.17
3.34 HDO
1.90 NMP
1.17
39.10 DMSO
1.90 NMP
1.90 NMP
1.17
1.17
1.37
1.37
1.23
1.37
1.37
1.37
1.37
1.37
0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 1.0 0.5
, ppm

[Fig 7]


H
N
CH2
6
H
N
O
O
O
O
n
PU control
PHU1 control
Compound D
Compound C
Storage Modulus [Pa]
Storage Modulus (Pa)
10^5
10^6
10^7
10^8
10^9
0.1
1
10
100
Frequency [Hz]
Frequency (Hz)
45% Humidity
65% Humidity
85% Humidity
OH
OH
O
O
CF3