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(54) Title: PROCESS FOR PREPARING POLYMER POLYOLS

(57) Abstract: The invention relates to a process for the preparation of a polymer polyol which is at most 60 wt.%, which process comprises mixing a base polyol, one or more ethylenically unsaturated monomers, a polymerization initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus obtained at a temperature of 50 to 200°C, optionally below 120 C, wherein the initiator is of formula R₁-C(=O)-O-O-R₂ (I) wherein R₁ is an alkyl group and R₂ is an alkyl group of formula -C(R₃)(R₄)-C(R₅)(R₆)(R₇) (II) wherein R₃ and R₄ are the same or different and are an alkyl group, R₅, R₆ and R₇ are the same or different and are a hydrogen atom or an alkyl group.



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PROCESS FOR PREPARING POLYMER POLYOLS

The present invention relates to a process for preparing polymer polyols having a solid polymer content which is at most 60 wt.%.

Polymer polyols are commonly used for the
5 manufacture of flexible polyurethane foams. Flexible
polyurethane foams are widely used in numerous
applications. Main sectors of application are automotive
and aircraft industry, upholstered furniture and
technical articles. For instance, full foam seats, top
10 pads for the seats and restraints for back and head, all
made from flexible polyurethane foam, are widely used in
cars and aeroplanes. Other applications include the use
of flexible polyurethane foam as carpet backings, bedding
and mattresses, foamed seat saddles for motorbikes,
15 gaskets between a car body and its lights, lip seals of
air filters for engines and insulating layers on car
parts and engine parts to reduce sound and vibration.

A problem generally encountered in the manufacture
of polymer polyols, that is to say a system wherein a
20 polymer is dispersed in a base polyol, is the production
of fouling.

In chemical processes where solid material is
produced, as in the present process, solids may form
within the reaction mixture and may adhere to the
25 interior walls of and any internals in the vessels
wherein the chemical processes take place. Such adhesion
can be so strong that after emptying the vessel, the
solid material forms a residue that remains adhered to
the interior walls. This solid material is known in the
30 field as fouling. In general, fouling comprises solid

material, sometimes in the form of a residue or coating, that is adhered to a surface. Portions of this fouling may become detached and become dispersed in the reaction mixture. Since the products of the present process are desirably stable dispersions of polymer particles within a polyol it will be appreciated that this loose fouling must also be removed, for example by filtration.

Especially in batch or semi-batch processes, it is desired that before a next batch is performed or after a certain number of batches, the fouling is removed as much as possible. In general, it is thought that fouling which is adhered to a surface reduces heat transfer through that surface.

A typical process for preparing a polymer polyol comprises mixing in a reactor vessel, a base polyol, one or more ethylenically unsaturated monomers, a polymerization initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus obtained at a temperature of 50 to 200 °C. Azobis(2-methylbutyronitrile), that is to say AMBN, is an initiator that is commonly used in the production of polymer polyols from ethylenically unsaturated monomer and base polyol. For example, WO199940144 discloses that suitable polymerization initiators in polymer polyol production include peroxide compounds and azo compounds, more specifically said AMBN.

Processes for the continuous production of polyol polymer compositions have been described previously that utilize a peroxide free-radical polymerization initiator (see US Patent No. 6455603 B; and International Patent Publication Nos. WO-A-00/00531 and WO-A-2008/005708). However, state of the art continuous processes require the presence of a preformed stabilizer. The preformed

stabilizer is typically formed during a polymerization reaction following addition of a precursor stabilizer compound, such as a vinyl alkoxy silane, to the mixture at the beginning of the process. The previously
5 described continuous processes also tend to operate at high temperatures, optimally in the region of 120°C to 140°C, most typically at around 130°C.

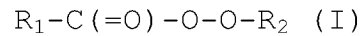
In continuous and batch polymer polyol production processes, fouling is formed on the interior surface of
10 the reactor vessel walls and any internals present in the reactor vessel. Such fouling can contribute to a reduction in effective heat transfer. Heat transfer is needed to heat the reactant mixture before initiation of polymerisation and to remove the heat of the
15 polymerisation reaction whilst it is underway. In batch processes, the reduced heat transfer results in a longer batch time. For example, the subsequent time increase for heating prior to the reaction for each batch results in fewer batches that can be performed within a defined
20 time period.

In polymer polyol preparation processes, it is known to remove fouling as adhered to the interior surface of the reactor vessel walls by using cleaning agents, such as acetone. Cleaning agents other than acetone for
25 removing such fouling have also been suggested in the art. For example, WO2010076259 discloses the use of an aqueous solution of a specific guanidine, including tetramethyl guanidine, in a batch process for preparing polymer polyols.

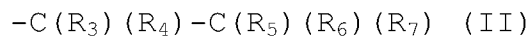
30 It is an object of the present invention to provide a polymer preparation process wherein the batch time increase from batch to batch is minimized or avoided completely. A reduced batch time increase would result

in a significant capacity increase for the reactor vessel and the process as a whole. In addition, it is also desirable to minimize the need for intervening cleaning steps between batches, which further reduce the efficiency of the process by increasing down-time.

Surprisingly, it has been found that incidence of fouling can be reduced significantly by undertaking the polymerization reaction at a temperature below about 120°C in the presence of a polymerization initiator of formula:

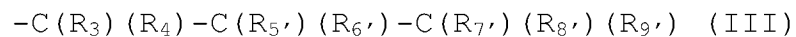


wherein R_1 is an alkyl group and R_2 is an alkyl group of formula



wherein R_3 and R_4 are the same or different and are an alkyl group, R_5 , R_6 and R_7 are the same or different and are a hydrogen atom or an alkyl group; or

where the polymerization initiator of formula (I) comprises an R_2 alkyl group of formula



wherein R_3 and R_4 are the same or different and are an alkyl group, R_5' and R_6' are the same or different and are a hydrogen atom or an alkyl group, R_7' , R_8' and R_9' are the same or different and are a hydrogen atom or an alkyl group, with the proviso that R_7' , R_8' and R_9' are not all hydrogen atoms in a case where both R_5' and R_6' are hydrogen atoms.

Accordingly in a first aspect the present invention

provides a process for the preparation of a polymer polyol having a solid polymer content which is at most 60 wt.%, which process comprises unsaturated monomers, a polymerization initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus obtained at a temperature of below 120°C, wherein the initiator is of formula (I) as described above.

In a second aspect the present invention provides a process for the preparation of a polymer polyol, which polymer polyol may have a solid polymer content which is at most around 60 wt.%, the process comprising mixing a base polyol, one or more ethylenically unsaturated monomers, a polymerization initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus obtained at a temperature of at least about 50°C to at most about 200°C, wherein the initiator is of the above formula (I) as described above.

In a specific embodiment of the invention the polymerization temperature is less than about 120°C, suitably less than 115°C, more suitably about 110°C or less.

Suitably, R₁ is an alkyl group having up to 10 carbon atoms, typically of from 4 up to 10 carbon atoms. Examples of suitable alkyl groups for R₁ are tert-butyl, 1-ethylpropyl, 1-ethylpentyl and 2,4,4-trimethylpentyl. In a specific embodiment of the present invention, R₁ is 1-ethylpentyl.

In relation to Formula (II), typically, R₃ and R₄ are an alkyl group having up to 10 carbon atoms, more suitably of from 1 up to 4 carbon atoms. R₃ and R₄ may be

selected from methyl or ethyl. In one embodiment of the invention, R_3 and R_4 are the same and are both methyl.

R_5 , R_6 and R_7 may all be a hydrogen atom in which case $-C(R_5)(R_6)(R_7)$ is a methyl group. Alternatively, at least one of R_5 , R_6 and R_7 is an alkyl group and may be selected from a methyl group, an ethyl group or a tertiary butyl group. In a specific embodiment of the invention both R_5 and R_6 are hydrogen atoms and R_7 is an alkyl group that has up to 10 carbon atoms, such as including a methyl, ethyl or tertiary butyl (tert-butyl)group.

In relation to Formula (III), typically, R_3 and R_4 are an alkyl group having up to 10 carbon atoms, more suitably of from 1 up to 4 carbon atoms. R_3 and R_4 may be selected from methyl or ethyl. In one embodiment of the invention, R_3 and R_4 are the same and are both methyl.

In a case where R_5' and R_6' are an alkyl group, the alkyl group preferably has up to 10 carbon atoms, more preferably of from 1 up to 4 carbon atoms. R_5' and R_6' may be methyl or ethyl.

In a case where one or more of R_7' , R_8' and R_9' are an alkyl group, the alkyl group has up to 10 carbon atoms, optionally at least 1 and up to 4 carbon atoms. R_7' , R_8' and R_9' may be methyl or ethyl. In a specific embodiment of the invention, R_7' , R_8' and R_9' are all the same and are methyl.

Examples of the R_2 alkyl groups of formula (II) are tertiary-butyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3-trimethylbutyl, 1,1,3,3-tetramethylbutyl, 1,1,2-trimethylpropyl, 1,1,2,2-tetramethylpropyl and 1,1,2,2-tetramethylbutyl. In an embodiment of the invention the R_2 alkyl group is 1,1,3,3-tetramethylbutyl.

In specific embodiments of the invention, R_1 and R_2

are alkyl groups containing no heteroatoms, such as oxygen, nitrogen and/or sulfur.

Examples of the R₂ alkyl groups of formula (III) include 1,1-dimethylbutyl, 1,1,3-trimethylbutyl, 1,1,3,3-tetramethylbutyl, 1,1,2-trimethylpropyl, 1,1,2,2-tetramethylpropyl and 1,1,2,2-tetramethylbutyl.

In a specific embodiment of the invention, the initiator is 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, that is to say a compound of formula (I) wherein R₁ is 1-ethylpentyl and R₂ is 1,1,3,3-tetramethylbutyl.

Use of said 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate in the production of polymer polyols is suggested in EP1624005. Said EP1624005 discloses a process for making a polymer polyol, comprising free-radical polymerizing a base polyol, a high potency preformed stabilizer, at least 1 ethylenically unsaturated monomer, at least 1 free-radical polymerization initiator, and a chain transfer agent. Said 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate is suggested as only 1 of many initiators that could be used in such process. Besides, EP1624005 additionally requires the presence of a preformed stabilizer and also that the polymer polyol be an "ultra-high solids" polymer polyol. As defined in EP1624005, "ultra-high solids" means that the content of solid polymer in the polymer polyol is greater than 60 wt.%. In addition, the reaction temperatures disclosed in said EP1624005 are broadly in excess of 120°C for initiators of the type used in the present invention.

In the present invention, the solid polymer content of the polymer polyol, which is the amount of solid polymer based on the total amount of polymer and polyol,

is at most 60 wt.%. Suitably, the solid polymer content is of from 25 to 55 wt.%. Preferably, the solid polymer content is of from 30 to 55 wt.%, more preferably of from 35 to 55 wt.%.

5 The present process may be a continuous, batch or semi-batch process. However, the present process works well as a batch or semi-batch process. In the latter case one or more compounds are added to the reactor continuously for a limited amount of time. Such
10 continuous addition may take place when adding the compounds to be mixed in an initial phase and/or when adding the compounds after such initial phase. Batch operation and semi-batch operation differ from continuous operation in that in batch and semi-batch operation the
15 product is removed from the reactor discontinuously. The fouling behaviour may vary between batch and continuous operation.

 The process of the present invention shows particular advantage in reducing the level of reactor
20 wall fouling that can result in a reduction in effective heat transfer during the polymerization reaction. It will be appreciated that in batch, semi-batch and continuous processes effective heat transfer is essential in order to ensure efficient operation (i.e. reduce the
25 need for increased energy consumption) as well as to maintain effective control of the reaction process. In an embodiment of the invention described in more detail below, in a batch process the batch-to-batch time
30 increase was reduced by nearly 60% when a polymerization initiator of formula I was used under reaction conditions of the invention. Further, the rate of filter replacement was also reduced by around one third when compared to processes using a different initiator.

In the present process, a polymer polyol is prepared by mixing a base polyol, one or more ethylenically unsaturated monomers, a polymerization initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus obtained at a temperature of 50 to 200°C. Processes for preparing polymer polyols are for example disclosed in WO1999040144, WO2003097712 and WO2008122581.

Such polymer polyol preparation is preferably carried out in a stainless steel reactor vessel. Further, preferably, the reactor vessel is a continuously stirred tank reactor, more preferably a stainless steel, continuously stirred tank reactor.

The temperature at which polymerization is carried out, is comprised in the range of from 50 to 200 °C, suitably 70 to 150 °C, more preferably 80 to 130 °C. In a specific embodiment of the invention the polymerization temperature is less than about 120°C, suitably less than 115°C, more suitably about 110°C or less. Further, it is preferred that during the entire polymerization process, the temperature is maintained constant at a certain value, with the proviso that a deviation of plus or minus 10 °C from said value is still allowable. Within said preferred embodiment, it is preferred that during the entire polymerization process, the temperature is maintained at a value comprised in the range of from about 70 to about 120 °C, preferably about 80 to about 115 °C.

The pressure at which polymerization may be carried out, is suitably comprised in the range of from 0.01 to 5 bar absolute, more suitably 0.05 to 4 bar absolute.

The base polyol used preferably is a polyether polyol, also frequently referred to as polyoxyalkylene

polyols. Such polyether polyols are typically obtained by reacting a starting compound having a plurality of active hydrogen atoms with one or more alkylene oxides, such as ethylene oxide, propylene oxide, butylene oxide or mixtures of two or more of these. Suitable polyether polyols are those having a nominal molecular weight in the range of from 350 to 15,000. In addition, the polyether polyols suitably have an average nominal functionality (Fn) of at least 2.0, typically greater than 2.0 and in one embodiment of the invention an average Fn of at least about 2.9. In a further embodiment of the invention it has been found particularly advantageous to use polyols having a molecular weight in the range of from 2000 to 14,000. Such polyols preferably further have a Fn greater than 2.5, and suitably in the range of from around 2.5 to around 3.0. The hydroxyl value of the polyol suitably has a value of from 10 to 150 mg KOH/g, more suitably of from 20 to 75 mg KOH/g. Examples of suitable polyols include CARADOL SC46-02, CARADOL SC36-13, CARADOL MC36-03, CARADOL SC56-02, CARADOL SC36-11, CARADOL SC48-03 and CARADOL MH56-03 (CARADOL is a trademark). Most preferably, CARADOL SC56-02 polyol and CARADOL SC48-03 polyol are used.

Suitable ethylenically unsaturated monomers for preparing the dispersed polymer include vinyl aromatic hydrocarbons, like styrene, alpha-methyl styrene, beta-methyl styrene and various other alkyl-substituted styrenes. Of these, the use of styrene is preferred. The vinyl aromatic monomer may be used alone or in combination with other ethylenically unsaturated monomers, such as acrylonitrile, methacrylonitrile, vinylidene chloride, various acrylates and conjugated

dienes like 1,3-butadiene and isoprene. Preferred ethylenically unsaturated monomers to be used for the purpose of the present invention are styrene and acrylonitrile in a weight ratio of from 30:70 to 100:0.

5 It is, however, particularly preferred to use styrene alone or a combination of styrene and acrylonitrile in a weight ratio styrene:acrylonitrile of from 50:50 to 75:25, resulting in dispersed polystyrene and styrene-acrylonitrile (SAN) copolymer, respectively.

10 Preferably, a macromer is fed when preparing the polymer polyol. Within the present specification, a macromer is considered to be a polyol which may contain one or more unsaturations and which purpose is to effect a stable dispersion of the polymer particles in the base polyol, said polymer particles obtained from polymerizing
15 one or more ethylenically unsaturated monomers.

Macromers which can be used include, but are not limited to the reaction product of a polyol with a reactive unsaturated compound such as maleic anhydride, phthalic
20 anhydride, fumaric acid, 1,1-dimethyl-m-isopropenyl-benzyl-isocyanate, isocyanatoethylmethacrylate, hydroxyethylmethacrylate, hydroxypropyl acrylate, methyl methacrylate, acrylic and methacrylic acid, methacryloyl chloride, glycidyl methacrylate and allyl glycidyl ether.
25 If a polycarboxylic acid or anhydride is employed, it is preferred to react the unsaturated polyol with an alkylene oxide. The polyol for preparing the macromer preferably has a hydroxyl functionality of at least 2.

A suitable macromer has been described in
30 WO199940144. Such macromer is suitable as a stabiliser precursor in a polymer polyol, and has been prepared by a process which comprises reacting a polyol with a cyclic dicarboxylic acid anhydride not containing any

polymerizable double bond, and subsequently reacting the adduct thus obtained with an epoxide compound containing a polymerizable double bond. The polyol preferably is sorbitol or a mixture of sorbitol with one or more diols (including water), said sorbitol or said mixture having reacted with a mixture of propylene oxide and ethylene oxide. The cyclic dicarboxylic acid anhydride preferably is phthalic anhydride. The epoxide compound preferably is glycidyl methacrylate or glycidyl acrylate. The adduct can first partly be reacted with a di- or higher functional epoxide compound before being reacted with the epoxide compound containing a polymerizable double bond. Further, the polyol can be reacted with a di- or higher functional isocyanate compound preceding the reaction between the polyol and the cyclic dicarboxylic acid anhydride. A method for preparing the macromer comprises reacting the adduct first partly with the epoxide compound containing a polymerizable double bond and subsequently reacting the reaction product thus obtained with a di- or higher functional epoxide compound or a di- or higher functional isocyanate compound.

The macromer suitably has a nominal molecular weight of at least 4000, typically in the range of from 5000 to 50,000.

The amount of ethylenically unsaturated monomers present during the process of the present invention can vary widely. At any time during the process according to the present invention, the amount of ethylenically unsaturated monomer will generally differ between of from 0 to 60% by weight based on total weight of base polyol, polymer, monomer(s) and optionally macromer. It is possible to have all base polyol fed initially, while it is also possible to add the majority of the base polyol

after initiation of polymerization.

The additional base polyol optionally added after initiation of polymerization can be the same or can be different from the base polyol as initially fed.

5 Preferably, the base polyol remains the same.

The polymerization initiator is usually applied in an amount of from 0.01 to 5% by weight based on total weight of monomers.

10 Chain transfer agents may also be added to or be present in the polymerization reaction medium. Preferably, they are fed to the reactor in the initial phase of the present process. The use of chain transfer agents and their nature is known in the art. Chain transfer agents enable a control of the molecular weight and/or the
15 cross-linking occurring between the various polymer molecules and hence may affect stability of the polymer polyol. If used at all, a chain transfer agent is suitably used in an amount of from 0.1 to 20% by weight, more suitably 0.2 to 10% by weight, and most suitably 0.3
20 to 7% by weight, based on total weight of end product.

Examples of suitable chain transfer agents are 1-butanol, 2-butanol, isopropanol, ethanol, methanol, cyclohexane and mercaptans, such as dodecanethiol, ethanethiol, 1-heptanethiol, 2-octanethiol and toluenethiol.

25 Preferably, isopropanol is used as a chain transfer agent.

Other compounds, such as compounds facilitating mixing of the various components, compounds which have a viscosity-lowering effect and/or compounds which enable
30 one or more of the components used to better dissolve in the reaction medium may also be applied. An example of a compound having a viscosity-lowering effect, thus enabling a better mixing of the components, is toluene.

Auxiliaries like toluene can be present in the feed and/or in the reactor.

5 A specific embodiment of the invention permits for the polymerization reaction to occur substantially in the absence of a preformed stabilizer. Preformed stabilizer is typically a small amount of a preformed copolymer of styrene, acrylonitrile and a macromer in the polymerization mixture that is formed separately and dosed into the reaction in order to stabilize the mixture. In this way the preformed stabilizer is a component that is added to the process as a separate ingredient. It is usually the reaction product of a macromer, in presence of styrene, acrylonitrile, and solvents/chain transfer agents like e.g. IPA, toluene and/or a polyol, and also a radical initiator. The preformed stabilizer is typically stored in a buffer tank/vessel from which it is dosed to the polymer polyol process. In the present invention it is not necessary to introduce one or more preformed stabilizer components to the reaction mixture prior to the polymerization step which represents a considerable advantage over previously known methods.

15 The present invention also relates to a polymer polyol, preferably a by-product free polymer polyol, obtainable by the process of the present invention.

20 The polymer polyol obtainable by the process of the present invention is very suitable for the preparation of polyurethane foams, especially flexible polyurethane foams, by reacting it with a suitable polyisocyanate in the presence of one or more suitable polyurethane catalysts, a suitable blowing agent, one or more surfactants, and optionally a cross-linking agent. This reaction is also commonly denoted as foaming. Therefore,

the present invention also relates to a process for preparing a polyurethane foam by foaming a composition comprising a polymer polyol obtainable by the process of the present invention and a polyisocyanate component.

5 Further, the present invention relates to a polyurethane foam obtainable by said foaming process. Still further, the present invention relates to a shaped article comprising said polyurethane foam.

10 Polyurethane catalysts are known in the art and include many different compounds. An extensive list of polyurethane catalysts is, for instance, given in U.S. patent specification No. 5,011,908. For the purpose of the present invention, suitable catalysts include tin-based catalysts, such as tin salts and dialkyl tin salts
15 of carboxylic acids. Specific examples are stannous octoate, stannous oleate, dibutyltin dilaureate, dibutyltin acetate and dibutyltin diacetate. Other suitable catalysts are tertiary amines, such as, for instance, bis(2,2'-dimethylamino)ethyl ether,
20 trimethylamine, triethylamine, triethylenediamine and dimethylethanolamine. Examples of commercially available tertiary amine catalysts are those sold under the tradenames NIAX, TEGOAMIN and DABCO (all trademarks). The catalyst is typically used in an amount of from 0.01
25 to 2.0 parts by weight per hundred parts by weight of polymer polyol (php). Preferred amounts of catalyst are from 0.05 to 1.0 php.

30 The use of cross-linking agents in the production of polyurethane foams is well known. Polyfunctional glycol amines are known to be useful for this purpose. The polyfunctional glycol amine which is most frequently used and is also useful in the preparation of the present flexible polyurethane foams, is diethanol amine, often

abbreviated as DEA or DEOA. If used at all, the cross-linking agent is applied in amounts up to 3.0 php, but amounts in the range of from 0.2 to 1.5 php are most suitably applied.

5 Suitable blowing agents include water, acetone, (liquid) carbon dioxide, halogenated hydrocarbons, aliphatic alkanes and alicyclic alkanes. Due to the ozone depleting effect of the fully chlorinated, fluorinated alkanes (CFC's) the use of this type of
10 blowing agents is generally not preferred, although it is possible to use them within the scope of the present invention. The halogenated alkanes, wherein at least one hydrogen atom has not been substituted by a halogen atom (the so-called HCFC's) have no or hardly any ozone
15 depleting effect and therefore are the preferred halogenated hydrocarbons to be used in physically blown foams. A very suitable HCFC type blowing agent is 1-chloro-1,1-difluoroethane. The use of water as a (chemical) blowing agent is also well known. Water
20 reacts with isocyanate groups according to the well known NCO/H₂O reaction, thereby releasing carbon dioxide which causes the blowing to occur. The aliphatic and alicyclic alkanes, finally, were developed as alternative blowing agents for the CFC's. Examples of such alkanes are n-
25 pentane and n-hexane (aliphatic) and cyclopentane and cyclohexane (alicyclic). It will be understood that the above blowing agents may be used singly or in mixtures of two or more. The amounts wherein the blowing agents are to be used are those conventionally applied, i.e. between
30 0.1 to 5 php in case of water and between about 0.1 and 20 php in case of halogenated hydrocarbons, aliphatic alkanes and alicyclic alkanes.
In addition, other well known auxiliaries, such as

flame retardants, foam stabilisers (surfactants) and fillers may also be used in the manufacture of polyurethane foams. Organosilicone surfactants are most conventionally applied as foam stabilisers in polyurethane production. A large variety of such organosilicone surfactants is commercially available. Usually, such foam stabiliser is used in an amount of up to 5% by weight based on the reaction mixture of polymer polyol reactant and polyisocyanate reactant.

10 The invention is further illustrated in the following non-limiting Examples.

Reference Example 1

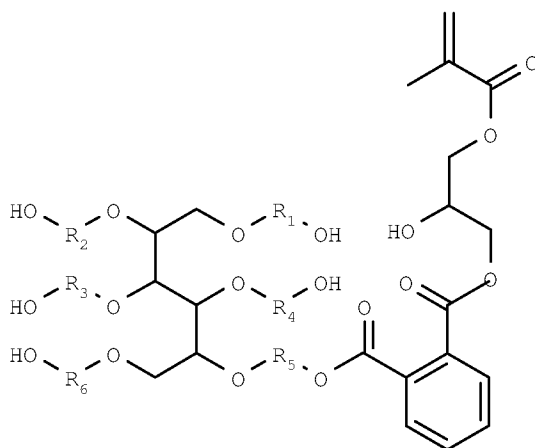
15 A polymer polyol was prepared by applying the following batch procedure, wherein the following compounds were used:

Base polyol = a polyether polyol containing randomly distributed ethyleneoxy and propyleneoxy monomers in the weight ratio of about 11/89. It was produced by using glycerol as the initiator and potassium hydroxide (KOH) as the catalyst. The base polyol had a weight average molecular weight of about 3,000 and had a OH value of about 54 mg KOH/g.

20 Styrene and acrylonitrile = ethylenically unsaturated monomers.

25 AMBN = azobis(2-methylbutyronitrile) (polymerization initiator).

Macromer = a polyol (in accordance with WO1999040144) having the following structure:



wherein R_1 to R_6 represent chains comprising randomly distributed propylene oxide (PO) and ethylene oxide (EO) monomers. The weight ratio of PO to EO in these chains was about 82/18. The weight average
 5 molecular weight per chain, averaged over all six chains, amounted to about 2,000.

IPA = isopropanol (chain transfer agent).

In the start-up phase of the batch, 182.5 g base polyol, 40.4 g macromer, 45.5 g IPA, 7.8 g styrene and
 10 2.8 g acrylonitrile were fed to a reactor. The reactor was a stainless steel, continuously stirred tank reactor. Further, heating of the contents of the reactor to 100 °C was performed. This heating was attained by external heating, with steam, of the reactor wall.

15 Once the contents of the reactor had a temperature of about 100 °C, the polymerisation was started by feeding 52.3 g of an 8 wt.% solution of the polymerization initiator AMBN in the base polyol, 296.3 g base polyol, 295.7 g styrene and 140.1 g acrylonitrile to
 20 the reactor. The polymerization temperature within the reactor was maintained at 100 °C.

Example 1

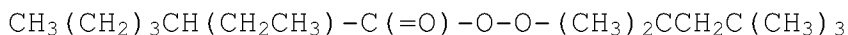
A polymer polyol was prepared by applying the following batch procedure.

In the start-up phase of the batch, 182.5 g base polyol, 40.4 g macromer, 45.5 g IPA, 7.8 g styrene and 2.8 g acrylonitrile were fed to a reactor. The reactor was a stainless steel, continuously stirred tank reactor. Further, heating of the contents of the reactor to 100 °C was performed. This heating was attained by external heating, with steam, of the reactor wall.

Once the contents of the reactor had a temperature of about 100 °C, the polymerisation was started by feeding 52.3 g of a 5 wt.% solution of a polymerization initiator in base polyol, 296.3 g base polyol, 295.7 g styrene and 140.1 g acrylonitrile to the reactor. The polymerization temperature within the reactor was maintained between 100 and 110 °C.

The base polyol and macromer were the same as the base polyol and macromer used in Reference Example 1.

The polymerization initiator was 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate. Such initiator is a compound of formula $R_1-C(=O)-O-O-R_2$ wherein R_1 is 1-ethylpentyl and R_2 is 1,1,3,3-tetramethylbutyl, that is to say a compound of the following formula:



Example 1 and Reference Example 1 on Large Scale

A batch procedure similar to the one as described above in Reference Example 1, using AMBN as the initiator, was performed on a large scale. After discharging the reactor content, a new batch procedure was started. For each batch procedure, the batch time increased as compared to the batch time of the preceding batch procedure. The average batch time increase for batches 6 to 34 was 0.92 minute (per batch).

Before change of the initiator, an acetone clean-out was performed in order to remove fouling as adhered to the interior walls of and internals in the reactor.

After said acetone washing, a batch procedure
5 similar to the one as described above in Example 1, using
1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate as the
initiator rather than AMBN, was performed on a large
scale. After discharging the reactor content, a new
batch procedure was started. For each batch procedure,
10 the batch time increased as compared to the batch time of
the preceding batch procedure. The average batch time
increase for batches 6 to 34 was only 0.39 minute (per
batch). This smaller average batch time increase as
compared to when using AMBN as the initiator (0.92 minute
15 as mentioned above) indicates that, surprisingly, less
fouling is produced when using 1,1,3,3-tetramethylbutyl
peroxy-2-ethylhexanoate as the initiator.

That less fouling is produced by the use of 1,1,3,3-
tetramethylbutyl peroxy-2-ethylhexanoate as the initiator
20 was also demonstrated by the effect on the number of
filter replacements. At the end of each of the above
batch procedures, the reactor content had to be
discharged. This was performed by passing the reactor
content through a filter and into another vessel. The
25 filter was used to remove any loose fouling that may be
present in the reactor content. This fouling is retained
by the filter. If there is too much fouling retained by
the filter, the polymer polyol product may no longer pass
through the filter, in which case the filter needed to be
30 replaced by a clean filter.

It has appeared that when using AMBN as the
initiator in the above batch procedures, 0.26 filters per
batch were required. On the other hand, when using

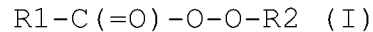
1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate as the initiator in the above batch procedures, only 0.17 filters per batch were required.

5 The solid polymer content of the polymer polyol product obtained after each of the above batch procedures, wherein the initiator was either AMBN or 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, was about 43 wt.%.

10 Although particular embodiments of the invention have been disclosed herein in detail, this has been done by way of example and for the purposes of illustration only. The aforementioned embodiments are not intended to be limiting with respect to the scope of the appended claims, which follow. It is contemplated by the
15 inventors that various substitutions, alterations, and modifications may be made to the invention without departing from the spirit and scope of the invention as defined by the claims.

C L A I M S

1. A process for the preparation of a polymer polyol having a solid polymer content which is at most 60 wt.%, which process comprises mixing a base polyol, one or more ethylenically unsaturated monomers, a polymerization
5 initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus obtained at a temperature of below 120°C, wherein the initiator is of formula



wherein R1 is an alkyl group and R2 is an alkyl
10 group of formula



wherein R3 and R4 are the same or different and are an alkyl group, R5, R6 and R7 are the same or different and are a hydrogen atom or an alkyl group.

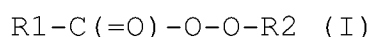
2. The process of claim 1, wherein R1 is an alkyl group
15 having up to 10 carbon atoms.

3. The process of claims 1 or 2, wherein at least one of R5, R6 and R7 is an alkyl group and is selected from a methyl group, an ethyl group or a tertiary butyl group

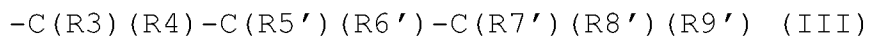
4. The process of any one of the preceding claims,
20 wherein R2 is selected from: tertiary-butyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3-trimethylbutyl, 1,1,3,3-tetramethylbutyl, 1,1,2-trimethylpropyl, 1,1,2,2-tetramethylpropyl or 1,1,2,2-tetramethylbutyl.

5. The process of claim 1, wherein the polymerization temperature is optionally less than about 115°C, more suitably about 110°C or less.

6. A process for the preparation of a polymer polyol
5 having a solid polymer content which is at most 60 wt.%, which process comprises mixing a base polyol, one or more ethylenically unsaturated monomers, a polymerization initiator, optionally a macromer, and optionally a chain transfer agent, and polymerizing the mixture thus
10 obtained at a temperature of 50 to 200°C, wherein the initiator is of formula



wherein R1 is an alkyl group and R2 is an alkyl group of formula



wherein R3 and R4 are the same or different and are an alkyl group, R5' and R6' are the same or different and are a hydrogen atom or an alkyl group, R7', R8' and R9' are the same or different and are a hydrogen atom or an alkyl group, with the proviso that R7', R8' and R9' are not all hydrogen atoms in a case where both R5' and R6' are hydrogen atoms.

7. The process of claim 6, wherein R1 is an alkyl group
15 having up to 10 carbon atoms.

8. The process of any one of claims 6 or 7, wherein R2 is 1,1-dimethylbutyl, 1,1,3-trimethylbutyl, 1,1,3,3-tetramethylbutyl, 1,1,2-trimethylpropyl, 1,1,2,2-tetramethylpropyl or 1,1,2,2-tetramethylbutyl.

9. The process of any of claims 6 to 8, wherein the polymerization temperature is below 120°C.

10. The process of any one of claims 1 to 9, wherein R2 is 1,1,3,3-tetramethylbutyl.

5 11. The process of any one of claims 1 to 10, wherein R1 is 1-ethylpentyl.

12. The process of any one of the preceding claims, wherein the base polyol has a nominal molecular weight in the range of from 350 to 15,000 and an average nominal
10 functionality (Fn) of greater than 2.0, optionally at least 2.9.

13. The process of any one of the preceding claims, wherein a macromer is used and the macromer is obtained by reacting a polyol with a cyclic dicarboxylic acid
15 anhydride not containing any polymerizable double bond, and subsequently reacting the adduct thus obtained with an epoxide compound containing a polymerizable double bond.

14. A process for preparing a polyurethane foam by
20 foaming a composition comprising a polymer polyol obtainable by the process according to any one of claims 1 to 13 and a polyisocyanate component.

15. A polyurethane foam obtainable by the process according to claim 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/063385

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08F283/06 C08F290/06 C08F2/00 C08F4/34 C08G18/63
 C08F283/04
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08F C08G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 00/00531 A1 (DOW CHEMICAL CO [US]; FOGG GRAEME D [NL]) 6 January 2000 (2000-01-06) cited in the application page 3, line 21 - page 5, line 16 page 6, line 19 - line 26 page 9, line 25 - line 32; claims; examples; table 1 ----- -/--	1-15

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
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Date of the actual completion of the international search 20 October 2011	Date of mailing of the international search report 27/10/2011
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Iraegui Retolaza, E
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/063385

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/005708 A1 (DOW GLOBAL TECHNOLOGIES INC [US]; VAN DER WAL HANNO R [CA]; DAWE ROBER) 10 January 2008 (2008-01-10) cited in the application page 2, line 28 - page 3, line 9 page 3, line 30 - page 4, line 7 page 8, line 15 - line 20 page 8, line 27 - page 9, line 4 page 11, line 11 - page 12, line 3; claims; examples B,2,3,5 page 16, line 1 - line 7 -----	1-15
X	US 6 455 603 B1 (FOGG GRAEME D [NL]) 24 September 2002 (2002-09-24) cited in the application	6-15
A	column 3, line 38 - line 49 column 5, line 44 - line 60; claim 6; examples -----	1-5
A	EP 0 439 755 A2 (BASF CORP [US]) 7 August 1991 (1991-08-07) page 4, line 45 - page 5, line 1; claims; examples -----	1-13
A	WO 2010/076259 A1 (SHELL INT RESEARCH [NL]; DENNEMAN MARCO ANTONIUS [NL]; KARZIJN WILLEM) 8 July 2010 (2010-07-08) cited in the application page 7, line 1 - line 10; claims 1,6 -----	1-15
A	WO 2008/122581 A1 (SHELL INT RESEARCH [NL]; BOUWMAN JEROEN PATRICK MICHEL [NL]; FENNIS PA) 16 October 2008 (2008-10-16) cited in the application page 10, line 20 - line 28; claims -----	1-15
A	EP 1 624 005 A1 (BAYER MATERIALSCIENCE LLC [US]) 8 February 2006 (2006-02-08) cited in the application paragraphs [0001], [0002], [0007], [0008], [0037], [0075] - [0078]; claim 8 -----	1-15
A	WO 03/097712 A1 (SHELL INT RESEARCH [NL]; HEINIS BOB [NL]; KARZIJN WILLEM [NL]; KRIJGER) 27 November 2003 (2003-11-27) page 7, line 31 - page 8, line 7; claims -----	1-13

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Information on patent family members

International application No

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