

1 MACROMER AND PROCESS FOR MAKING POLYMER POLYOLS
2

3 This invention relates to methods for making dispersions of polymer particles in
4 a polyol.

5 “Polymer polyols” (sometimes known as “copolymer polyols”) are widely used raw
6 materials for manufacturing flexible polyurethane foam and other polyurethane
7 products. They have a continuous phase made up of one or more compounds having
8 multiple hydroxyl groups (*i.e.*, a “polyol”) into which another polymer is dispersed in the
9 form of small particles. The dispersed polymer particles help to form open cells and to
10 increase the load-bearing of polyurethane foam that is made with the polymer polyol.

11 Stability is an important characteristic of polymer polyols. If the dispersion is
12 unstable, some or all of the dispersed polymer phase can settle out as the polymer polyol
13 is stored, transported and used. This leads to fouling of transportation, storage and
14 processing equipment, inconsistencies in the polymer polyol product and inconsistencies
15 in polyurethanes made from the polymer polyol.

16 Stability is improved through the use of stabilizers. The stabilizer contains
17 polyol-soluble groups, typically polyether chains which can have molecular weights up to
18 several thousand. Some or all of the stabilizer resides at the surface of the dispersed
19 polymer particles, where the polyol-soluble groups are believed to stabilize the particles
20 through the interaction of these polyol-soluble groups with the continuous polyol phase.

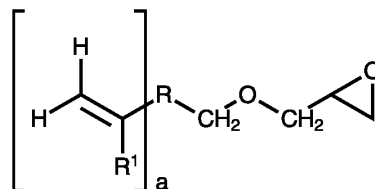
21 One common type of stabilizer is a “macromer” compound, typically a polyether
22 polyol in which one or more of the hydroxyl groups are capped with a group that
23 contains polymerizable unsaturation. Those unsaturated stabilizers can copolymerize
24 with the vinyl monomers used to make the dispersed polymer particles, thereby grafting
25 the stabilizer directly to the particles. The capping group is almost always an
26 ethylenically unsaturated polyisocyanate such as 3-isopropenyl- α,α -
27 dimethylbenzylisocyanate (TMI) or isocyanatoethylmethacrylate (IEM). Other types of
28 capping agents include halides such as vinyl benzyl chloride and ethylenically
29 unsaturated siloxanes such as vinyltrimethoxysilanes.

30 A shortcoming associated with the use of these isocyanate capping agents is they
31 are very reactive with water, including atmospheric moisture, and tend to form amine
32 and urea by-products during storage and handling. The amine and urea by-products are
33 not useful stabilizer compounds and do not react with polyols to form stabilizer

1 compounds. Stabilizers made from the isocyanate capping agents tend to be
 2 inconsistent in their composition and their performance. Polymer polyols made from
 3 these stabilizers are often less stable than is wanted. The presence of the amine and
 4 urea by-products also can interfere with the processing of the polymer polyols to produce
 5 polyurethane foam. It would be desirable to avoid these problems.

6 Epoxide compounds have been suggested for use in producing stabilizers for
 7 polymer polyols. *See, e.g.*, US 9,994,701, which mentions without further elaboration
 8 the possibility of using an unsaturated epoxide as a capping agent. US 5,059,641
 9 describes epoxide-modified polyols as being useful stabilizers, but in this case neither
 10 the epoxide compound nor the stabilizer is unsaturated, and the stabilizer cannot
 11 copolymerize with the vinyl monomers during the manufacturing process.

12 In one aspect, this invention is a process for making a polymer polyol, comprising
 13 polymerizing one or more low molecular weight ethylenically unsaturated monomers
 14 that have a molecular weight of no greater than 150 in a continuous liquid polyol phase
 15 and in the presence of a stabilizer to form a dispersion of solid polymer particles in the
 16 continuous liquid polyol phase, wherein the stabilizer includes (i) a macromer produced
 17 in a reaction of a hydroxyl-containing polyether with an epoxide compound having a
 18 polymerizable carbon-carbon double bond; (ii) a pre-formed polymer formed by
 19 polymerizing a carbon-carbon double bond of such macromer, or (iii) a mixture of (i) and
 20 (ii), wherein the epoxide compound is represented by structure I:



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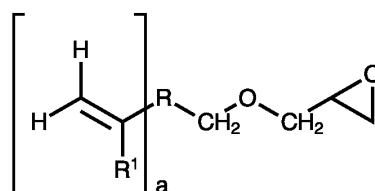
21 where a is a positive number, R is a covalent bond or an organic linking group and R¹ is
 22 hydrogen or hydrocarbyl group having up to 6 carbon atoms. These epoxide compounds
 23 can be understood as corresponding to a glycidyl ether of a CH₂=CHR¹-R-CH₂-OH
 24 compound.
 25

26 The applicant has found that many types of unsaturated epoxide compounds are
 27 unsuitable for use in making a macromer or stabilizer. Epoxy compounds which have
 28 two methylene groups bonded directly to the ether oxygen shown structure I have been

found to exhibit good reactivity with a hydroxyl-containing polyether while engaging in few if any unwanted side-reactions. The resulting macromer also polymerizes well during the formation of a pre-formed polymer and/or during the polymerization step that produces the polymer polyol.

In certain embodiments the stabilizer includes an unsaturated macromer. The macromer is a reaction product of a hydroxyl-containing polyether with an epoxide compound as described above. An alcohol group of the polyether reacts with the epoxide group of the epoxide compound in a ring-opening reaction to form an ether linkage. This introduces to the polyether a capping group that contains polymerizable carbon-carbon unsaturation. A hydroxyl group forms as a result of the opening of the epoxide ring.

The epoxide compound is represented by structure I:

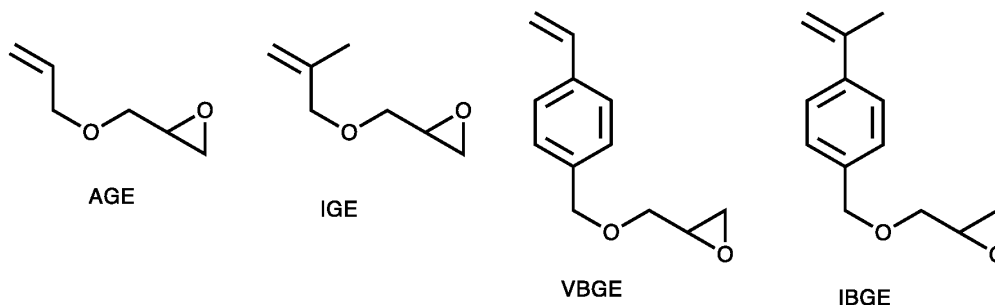


(I)

where a is a positive number, R is a covalent bond or an organic linking group and R^1 is hydrogen or hydrocarbyl group having up to 6 carbon atoms. These epoxide compounds can be understood as corresponding to a glycidyl ether of a $CH_2=CHR^1-R-CH_2-OH$ compound. R is preferably a covalent bond, linear or branched alkylene having up to 12 (such as 1-6) carbon atoms, phenylene, or an alkyl-substituted phenylene having up to 12 carbon atoms. a preferably is one. R^1 is preferably methyl or hydrogen. The epoxide compound may have a molecular weight of, for example, up to 500, up to 300, up to 250 or up to 170.

In some embodiments, R is a covalent bond or phenylene, R^1 is methyl or hydrogen and a is one. In such embodiments the epoxide compound may be an allyl glycidyl ether, an isopropenyl glycidyl ether, a glycidyl ether of a vinyl aromatic compound or a glycidyl ether of an isopropenyl aromatic compound.

Examples of useful epoxide compounds include vinyl benzyl glycidyl ether (VBGE), isopropenyl benzyl glycidyl (IBGE) ether, allyl glycidyl ether (AGE) and isopropenyl glycidyl ether (IGE), which have the following respective structures:



Of these, VBGE is more preferred. Many unsaturated epoxide compounds have been found to be unsuitable for forming a macromer, for various reasons. In some cases, the unsaturated epoxide compound reacts sluggishly with the polyether so little macromer is produced. Divinylbenzene monoxide is an example of such a poorly-reacting epoxide compound. Other compounds such as isopropenylphenyl glycidyl ether may engage in unwanted side reactions, in addition to being poorly reactive with the polyether. Glycidyl ethers of structure I have been found to have desirable reactivity and to engage in few unwanted side-reactions. These produce the wanted macromer in good yields. These epoxide compounds are very unreactive with atmospheric moisture. VBGE and AGE have the further advantages of being room temperature liquids.

The polyether may be, for example, a polymer of any one or more of ethylene oxide, propylene oxide, 1,2-butylene oxide, 1,3-butylene oxide, tetrahydrofuran, cyclohexane oxide, epichlorohydrin and styrene oxide. A preferred polyether is a homopolymer of propylene oxide or a random and/or block copolymer of propylene oxide and ethylene oxide. In a particular embodiment, the polyether is a random copolymer of 80 to 95% by weight propylene oxide and 5 to 20% ethylene oxide, especially a random copolymer of 84 to 90% by weight propylene oxide and 10 to 16% by weight ethylene oxide. For purposes of this invention, a copolymer of propylene oxide and ethylene oxide is considered to be "random" if the propylene oxide and ethylene oxide are provided to the polymerization in the aforementioned proportions and polymerized simultaneously.

The polyether before reaction with the epoxide compound may have one or more hydroxyl groups. It may have, for example, 2 to 16, 2 to 12, 2 to 8 or 4 to 8 hydroxyl groups.

The hydroxyl equivalent weight of the polyether before reaction with the epoxide compound may be, for example, at least 300, at least 500, at least 1000 or at least 1500,

1 and may be, for example, up to 3000, up to 2500 or up to 2000. Equivalent weight is
2 conveniently determined using titration methods per ASTM 4274-88 or equivalent,
3 converting the measured hydroxyl number in mg KOH/g to equivalent weight using the
4 relationship: Equivalent Weight = 56,100 ÷ hydroxyl number. The molecular weight of
5 the polyether may be, for example, at least 300, at least 1000, at least 2500, at least
6 5000, at least 6000, at least 8000 or at least 11,000 g/mol and, for example, up to 25,000,
7 up to 15,000 or up to 14,000 g/mol. Molecular weights as reported herein are number
8 averages as determined using gel permeation chromatography methods, against a
9 polystyrene standard.

10 The polyether prior to reaction with the epoxide compound preferably contains no
11 more than 0.2 milliequivalents per gram of terminal unsaturation, as measured
12 according to ASTM 4671-16.

13 The epoxide compound and polyether can be reacted at a ratio of, for example, up
14 to 1 mole of epoxide compound per equivalent of hydroxyl groups provided by the
15 polyether. A preferred ratio is up to 1.25 or up to 1 mole of epoxide compound per mole
16 of polyether, to minimize the formation of macromer compounds that have two or more
17 carbon-carbon double bonds. An especially preferred ratio is 0.2 to 0.8 or 0.25 to 0.6
18 moles of the epoxide compound per mole of the polyether.

19 The product of the reaction of epoxide compound and polyether is a macromer
20 having a polyether portion and an average at least one terminal group having a
21 polymerizable carbon-carbon double bond corresponding to that of the starting epoxide
22 compound. By "polymerizable", it is meant that the double bond can polymerize with
23 carbon-carbon double or triple bonds of other molecules (including other macromer
24 molecules and the low molecular weight ethylenically unsaturated monomers described
25 herein) to form a polymer. The macromer preferably has an average of 1 to 2, more
26 preferably 1 to 1.5, polymerizable carbon-carbon double bonds per molecule.

27 Some portion of the starting polyether may remain unreacted, especially when
28 less than one mole of epoxide compound is used per mole of epoxide compound. It is
29 generally unnecessary to separate the macromer from unreacted polyether before using
30 the macromer to manufacture a polymer polyol.

31 The macromer may contain one or more hydroxyl groups. In some embodiments,
32 the macromer contains at least one, at least 2 or at least 3 hydroxyl groups per

1 molecule. In particular embodiments the macromer contains 3 to 8, 4 to 7 hydroxyl or 4
2 to 6 hydroxyl groups per molecule.

3 The molecular weight of the macromer is generally equal to that of the polyether
4 plus that of the group introduced in the capping reaction. The number average
5 molecular weight of the macromer may be, for example, at least 500, at least 1250, at
6 least 2750, at least 5250, at least 6250, at least 8250 or at least 11,250 g/mol and, for
7 example, up to 26,000, up to 16,000 or up to 15,000 g/mol.

8 In specific embodiments, the polyether portion of the macromer is a random
9 copolymer of a mixture of 84 to 90% by weight propylene oxide and 10 to 16% by weight
10 ethylene oxide, having a molecular weight of 8,000 to 15,000 g/mol and more preferably
11 11,000 to 14,000 g/mol, and the macromer contains 3 to 7 hydroxyl groups per molecule
12 and 1 to 1.5 polymerizable unsaturated groups per molecule. In other specific
13 embodiments, the polyether portion of the macromer is a random copolymer of a mixture
14 of 85 to 90% by weight propylene oxide and 10 to 15% by weight ethylene oxide, having
15 a molecular weight from 10,000 to 15,000 g/mol, and the macromer contains 4 to 6
16 hydroxyl groups per molecule and 1 to 1.5 polymerizable unsaturated groups per
17 molecule.

18 The epoxide compound and polyether are combined and subjected to conditions
19 under which at least one hydroxyl group of the polyether reacts with an epoxide ring of a
20 molecule of the epoxide compound, opening the epoxide ring and forming an ether bond
21 to one of the ring carbon atoms. A hydroxyl group is produced in this reaction. Suitable
22 reaction conditions include a temperature of 0 to 200°C and a pressure such that the
23 starting materials do not boil. The reaction preferably is performed under an inert
24 atmosphere such as nitrogen, helium or argon, and in the absence of free radicals or
25 other conditions such as would induce polymerization of the carbon-carbon double
26 bonds.

27 The reaction may be catalyzed. Examples of useful catalysts include alkali metal
28 hydroxides, alkali metal alkoxides and Lewis acids. Alkali metal hydroxide and alkali
29 metal alkoxide catalysts are of particular interest because the polyether may be
30 prepared by polymerizing one or more alkylene oxides in the presence of an alkali metal
31 hydroxide or alkali metal alkoxide. Typically the polyether is neutralized at the end of
32 the polymerization step to convert terminal $-O^-M^+$ moieties (M representing the alkali
33 metal) to hydroxyl groups. An advantage of catalyzing the reaction with an alkali metal

1 hydroxide or alkoxide is that the reaction of the polyether and epoxide compound can be
2 performed before the polyether has been neutralized. Instead, the polyether is produced
3 in a polymerization using an alkali metal hydroxide or alkali metal alkoxide
4 polymerization catalyst and, without neutralizing the resulting polyether, combining the
5 polyether with an epoxide compound of structure I, and reacting them to produce the
6 macromer. The macromer then can be neutralized. This can be performed in the same
7 vessel or equipment in which the polyether is polymerized

8 The time required for the reaction may be, for example, from 1 minute to 24
9 hours.

10 The stabilizer of the invention includes the macromer as just described, and/or a
11 preformed polymer of such a macromer. Such a pre-formed polymer may be formed by
12 homopolymerizing the macromer or by copolymerizing the macromer with one or more
13 other ethylenically unsaturated monomers having a molecular weight of up to 150. The
14 preformed polymer may have a number average molecular weight from 30,000 to
15 1,000,000 g/mol as measured by gel permeation chromatography against a polystyrene
16 standard, and an average of 1 to 20 pendant polyether chains per molecule. It may be a
17 block or random copolymer of the macromer and one or other ethylenically unsaturated
18 monomers having a molecular weight of up to 150.

19 A useful comonomer for making the pre-formed polymer of the macromer is
20 styrene, although other vinyl aromatic monomers and/or one or more acrylate esters,
21 one or more methacrylate esters, acrylonitrile and the like are suitable. The amount of
22 low molecular weight monomer (when used to make the macromer) may range from, for
23 example, 0.1 to 10 parts by weight per part by weight of macromer, and more preferably
24 from 1 to 5 parts by weight per part by weight of macromer.

25 The polymerization or copolymerization of the macromer to form the pre-formed
26 polymer may be performed in a free-radical polymerization, including in a "controlled
27 radical polymerization", by which is meant a living free-radical polymerization process
28 characterized in that a dynamic equilibrium between propagating radicals and dormant
29 species is established, allowing radicals to become reversibly trapped. Various types of
30 controlled radical polymerizations are known including, for example, cobalt-mediated
31 radical polymerization (CMRP), stable free radical mediated polymerization (SFRMP)
32 (including, for example, a nitroxide-mediated polymerization (NMP)), atom transfer
33 radical polymerization (ATRP) and reversible addition fragmentation chain transfer

1 (RAFT). Preferred processes are the RAFT and nitroxide-mediated polymerization
2 processes.

3 The polymerization of the macromer to form the pre-formed polymer can be
4 performed in bulk, but may instead be performed as a mixture or dispersion in a carrier.
5 The carrier may constitute up to about 80%, preferably about 20 to 80% and more
6 preferably about 50 to 80%, of the combined weight of the carrier, macromer and low
7 molecular weight monomers (if any). The carrier material may include, for example, a
8 polyether polyol such as, for example, an uncapped portion of the random copolymer
9 used in preparing the macromer.

10 Alternatively or in addition, the carrier may include one or more low molecular
11 weight compounds having a molecular weight of about 250 or less, which are not
12 polyethers and are not copolymerizable with the macromer, and which are solvents for
13 the low molecular weight monomer(s). Suitable carriers of this type include aromatic
14 hydrocarbons such as toluene or xylene, aliphatic hydrocarbons such as hexane,
15 monoalcohols such as ethanol and isopropanol, and ketones such as acetone. If such a
16 low molecular weight compound is used as all or part of the carrier, it should be
17 removed before, during or after the time that the pre-formed polymer is used to make
18 the polymer polyol. Similarly, residual monomers and other volatile polymerization by-
19 products can be removed from the pre-formed polymer before, during or after the time
20 the polymer polyol is prepared. These materials can be removed by subjecting the pre-
21 formed polymer or the polymer polyol to reduced pressures and/or elevated
22 temperatures, or by various other stripping methods.

23 In the polyol polyol manufacturing process of this invention, one or more low
24 molecular weight ethylenically unsaturated monomers that have a molecular weight of
25 no greater than 150 are polymerized in a continuous liquid polyol phase and in the
26 presence of a stabilizer as described herein, *i.e.*, a macromer as described above and/or a
27 pre-formed polymer thereof. From 1.5 to 15% by weight of the stabilizer of the invention
28 is present, based on the weight of the low molecular weight monomers. A preferred
29 amount is from 2 to 10% by weight and a still more preferred amount is 2 to 8% by
30 weight, based on the weight of the low molecular weight monomers.

31 Additional stabilizers can be present in addition to the macromer and/or pre-
32 formed polymer of this invention. However, it is preferred that the macromer and/or
33 pre-formed polymer thereof constitute at least 50%, preferably at least 75%, more

1 preferably at least 90% of the total weight of all stabilizers. The macromer and/or pre-
2 formed polymer may be the only stabilizer(s) present. An advantage of this invention is
3 that very good results are achieved when the macromer is used as the stabilizer without
4 prior polymerization. Therefore, in preferred embodiments, the macromer is not formed
5 into a preformed polymer, and the macromer constitutes at least 50%, at least 75%, at
6 least 95% of the weight of all the stabilizers. It may constitute up to 100% of the weight
7 of all stabilizers.

8 Suitable methods of producing polymer polyols include those described, for
9 example, in USP 4,513,124, USP 4,588,830, USP 4,640,935, USP 5,854,386, USP
10 4,745,153, USP 5,081,180, USP 6,613,827 and EP 1 675 885, modified by using the
11 stabilizer of this invention. In general, these methods include dissolving the low
12 molecular weight monomer(s) in a polyol and in the presence of the stabilizer, and
13 subjecting the dissolved monomer to polymerization conditions until the polymer chains
14 precipitate and are converted to solid polymer particles dispersed in a continuous polyol
15 phase.

16 Examples of useful low molecular weight monomers include, for example,
17 aliphatic conjugated dienes such as butadiene and isoprene; monovinylidene aromatic
18 monomers such as styrene, α -methyl styrene, t-butyl styrene, chlorostyrene,
19 cyanostyrene and bromostyrene; α,β -unsaturated carboxylic acids, and esters or
20 anhydrides thereof such as acrylic acid, methacrylic acid, methyl methacrylate, ethyl
21 acrylate, 2-hydroxyethyl acrylate, butyl acrylate, itaconic acid, maleic anhydride and the
22 like; α,β -unsaturated nitriles and amides such as acrylonitrile, methacrylonitrile,
23 acrylamide, methacrylamide, N,N-dimethyl acrylamide, N-(dimethylaminomethyl)
24 acrylamide and the like; vinyl esters such as vinyl acetate, vinyl ethers, vinyl ketones,
25 vinyl and vinylidene halides, and the like. Monovinylidene aromatic monomers such as
26 styrene and ethylenically unsaturated nitriles such as acrylonitrile are preferred.
27 Especially preferred are mixtures of styrene and acrylonitrile; such a mixture may
28 contain, for example, 50 to 90% by weight styrene and 10 to 50% by weight acrylonitrile.

29 The polyol that forms the continuous phase in the polymer polyol product is an
30 organic material or mixture of organic materials that is a liquid at room temperature
31 (23°C) and which contains an average of at least 1.5 isocyanate-reactive groups per
32 molecule. For purposes of this invention, the term "polyol" is used as a shorthand term
33 for such materials, even though the actual isocyanate-reactive groups in a particular

1 case may not necessarily be hydroxyl groups. Also for purposes of this invention, the
2 macromer or preformed polymer of the macromer is not considered as part of the polyol.
3 The liquid polyol preferably contains an average of 1.8 to 8 isocyanate-reactive
4 groups/molecule, especially from 2 to 4 such groups. The isocyanate-reactive groups are
5 preferably aliphatic hydroxyl, aromatic hydroxyl, primary amino and/or secondary
6 amino groups. Hydroxyl groups are preferred. Hydroxyl groups are preferably primary
7 or secondary hydroxyl groups.

8 The equivalent weight of the polyol per isocyanate-reactive groups will depend on
9 the intended applications. Polyols having an equivalent weight of 400 or greater, such
10 as from 400 to 3000, are preferred for forming elastomeric polyurethanes such as
11 slabstock or molded polyurethane foams, microcellular polyurethane elastomers and
12 non-cellular polyurethane elastomers. Lower equivalent weight polyols, such as those
13 having an equivalent weight of 31 to 399, are preferred for making rigid polyurethane
14 foams and structural polyurethanes.

15 Preferred types of liquid polyol(s) include polyether polyols, polyester polyols, and
16 various types of polyols that are prepared from vegetable oils or animal fats.

17 Polyether polyols include, for example, polymers of propylene oxide, ethylene
18 oxide, 1,2-butylene oxide, tetramethylene oxide, block and/or random copolymers
19 thereof, and the like. Of particular interest are poly(propylene oxide) homopolymers;
20 random copolymers of propylene oxide and ethylene oxide in which the poly(ethylene
21 oxide) content is, for example, from about 1 to about 30% by weight; ethylene oxide-
22 capped poly(propylene oxide) polymers; and ethylene oxide-capped random copolymers
23 of propylene oxide and ethylene oxide. The polyether polyols may contain low levels of
24 terminal unsaturation (for example, less than 0.02 meq/g or less than 0.01 meq/g).
25 Examples of such low unsaturation polyether polyols include those made using so-called
26 double metal cyanide (DMC) catalysts, as described for example in US Patent Nos.
27 3,278,457, 3,278,458, 3,278,459, 3,404,109, 3,427,256, 3,427,334, 3,427,335, 5,470,813
28 and 5,627,120. Polyester polyols typically contain about 2 hydroxyl groups per molecule
29 and have an equivalent weight per hydroxyl group from about 400 to 1500. An
30 uncapped polyether from the macromer-forming reaction may form all or part of the
31 polyol.

32 Suitable polyesters include reaction products of polyols, preferably diols, with
33 polycarboxylic acids or their anhydrides, preferably dicarboxylic acids or dicarboxylic

1 acid anhydrides. Other suitable polyesters include polymers of cyclic lactones such as
2 polycaprolactone.

3 Suitable polyols prepared from vegetable oils and animal fats include for
4 example, hydroxymethyl group-containing polyols as described in WO 04/096882 and
5 WO 04/096883; castor oil, so-called "blown" vegetable oils, and polyols prepared by
6 reacting a vegetable oil with an alkanolamine (such as triethanolamine) to form a
7 mixture of monoglycerides, diglycerides, and reaction products of the fatty acid amides,
8 which are ethoxylated to increase reactivity and to provide a somewhat more
9 hydrophilic character. Materials of the last type are described, for example in
10 GB1248919.

11 Suitable low equivalent weight polyols include materials that are not
12 copolymerizable with the stabilizer and which contain 2 to 8, especially 2 to 6 hydroxyl,
13 primary amine or secondary amine groups per molecule and have a hydroxyl equivalent
14 weight from 30 to about 200, especially from 50 to 125. Examples of such materials
15 include diethanol amine, monoethanol amine, triethanol amine, mono- di- or
16 tri(isopropanol) amine, glycerin, trimethylolpropane, trimethylolethane, pentaerythritol,
17 sorbitol, ethylene glycol, diethylene glycol, 1,2-propylene glycol, dipropylene glycol,
18 tripropylene glycol, ethylene diamine, phenylene diamine, bis(3-chloro-4-
19 aminophenyl)methane and 2,4-diamino-3,5-diethyl toluene.

20 In the polymerization, the amount of low molecular weight monomers may range
21 from 5 to 65%, preferably 15 to 55% and more preferably from 35 to 50%, by weight of
22 all components of the reaction mixture. The "solids" of the product, *i.e.* the weight
23 percentage of solid polymer particles in the product, is in general considered to be the
24 same as the weight percentage of low molecular weight monomers present in the
25 polymerization process, assuming essentially complete (95% or more) conversion of
26 monomers to polymer, which is typical. The polyol(s) that form the continuous polyol
27 phase may constitute 10 to 94%, preferably 30 to 70%, more preferably 40 to 60% by
28 weight, based on the weight of the product.

29 Various other ingredients may be present during the polymer polyol production
30 process, in addition to the polyol(s), low molecular weight monomer(s) and stabilizer(s).
31 A polymerization catalyst preferably is present. The polymerization catalyst preferably
32 is a free radical initiator that generates free radicals under the conditions of the
33 polymerization process. Examples of suitable free-radical initiators include, for

1 example, peroxy compounds such as peroxides, persulfates, perborates, percarbonates;
2 azo compounds and the like. Specific examples include hydrogen peroxide,
3 di(decanoyl)peroxide, dilauroyl peroxide, t-butyl perneodecanoate, 1,1-dimethyl-3-
4 hydroxybutyl peroxide-2-ethyl hexanoate, di(t-butyl)peroxide, t-butylperoxydiethyl
5 acetate, t-butyl peroctoate, t-butyl peroxy isobutyrate, t-butyl peroxy-3,5,5-trimethyl
6 hexanoate, t-butyl perbenzoate, t-butyl peroxy pivalate, t-amyl peroxy pivalate, t-butyl
7 peroxy-2-ethyl hexanoate, lauroyl peroxide, cumene hydroperoxide, t-butyl
8 hydroperoxide, azo bis(isobutyronitrile), 2,2'-azo bis(2-methylbutyronitrile) and the like.
9 Two or more catalysts may be used. The amount of catalyst may range from 0.01 to 5%,
10 preferably 0.01 to 3% by weight, based on the weight of the low molecular weight
11 monomer(s).

12 A molecular weight regulator such as a chain transfer agent is another useful
13 ingredient. Examples of these include low molecular weight aliphatic alcohols such as
14 isopropanol, ethanol and t-butanol; toluene; ethylbenzene; certain tertiary amines such
15 as triethylamine; mercaptans such as n-dodecylmercaptan and octadecylmercaptan; and
16 chlorinated alkanes such as carbon tetrachloride, carbon tetrabromine, chloroform,
17 methylene chloride and the like. These materials are typically present (if used at all) in
18 amounts ranging from 0.01 to 3%, preferably 0.25 to 2%, based on the weight of the low
19 molecular weight monomers.

20 It is often beneficial to provide seed particles in the polymerization. The seed
21 particles are solid particles of an organic polymer; the organic polymer most preferably
22 is a polymer of one or more of the same low molecular weight monomers used in the
23 polymerization. The seed particles may have any convenient particle size up to the
24 target particle size for the polymerization. The seed particles are most conveniently
25 provided in the form of a dispersion of the particles in a polyol phase. Such a dispersion
26 can be specially made. However, a seed dispersion can be simply a portion of a
27 previously-made polymer polyol, such as, for example, a portion of a previously made
28 batch of the same polymer polyol product. In industrial batch or semi-batch processes, a
29 reactor "heel", *i.e.*, a small portion of a previously made batch of copolymer polymer that
30 remains in the reaction vessel after removal of the product, is a useful source of seed
31 particles. The seed particles preferably constitute up to 5%, preferably up to 2% and
32 more preferably up to 1%, of the weight of the product polymer polyol. If the seed
33 particles are provided in the form of a seed dispersion, the seed dispersion may

1 constitute up to 10%, preferably up to 5% and more preferably up to 3% of the total
2 weight of the product polymer polyol.

3 The polymerization typically is performed at an elevated temperature, below the
4 temperature at which any of the polyol(s) and/or low molecular weight monomers boils
5 under the pressure conditions used, typically from 80 to 200°C, more typically 100 to
6 140°C, still more typically from 110 to 130°C. The free radical initiator may be selected
7 in conjunction with the selection of polymerization temperature, so the free radical
8 initiator decomposes to produce free radicals at the polymerization temperature.

9 The polymerization typically is performed under agitation to keep the low
10 molecular weight monomers dispersed in the form of small droplets in the polyol phase
11 until they have polymerized to form solid particles. The polymerization is continued
12 until solid polymer particles are formed and preferably until at least 90%, more
13 preferably at least 95% by weight of the low molecular weight monomers have become
14 converted to polymer. During the polymerization, the macromer and/or pre-formed
15 polymer thereof may in some cases copolymerize with the low molecular weight
16 monomer(s) to graft the macromer or pre-formed polymer thereof to the dispersed
17 polymer particles.

18 The polymerization can be performed continuously, or in various batch and semi-
19 batch processes. A continuous process is characterized by the continuous introduction of
20 polyol(s), stabilizer, and low molecular weight monomers into the polymerization, and
21 continuous withdrawal of product. In a semi-batch process, at least a portion of the low
22 molecular weight monomers is continuously or intermittently introduced into the
23 polymerization, but product is not continuously withdrawn, preferably not being
24 removed until the polymerization is completed. In the semi-batch process, some or all of
25 the polyol(s) and/or stabilizer may be added continuously or intermittently during the
26 process, but the entire amounts of those materials may instead be charged to the
27 polymerization apparatus prior to the start of the polymerization. In a batch process, all
28 polyol(s), stabilizer(s) and low molecular weight monomers are charged at the beginning
29 of the polymerization, and product is not removed until the polymerization is completed.

30 After the polymerization is completed, the product may be subjected to
31 operations such as the removal of volatiles (such as residual monomers and/or other low
32 molecular weight materials). Volatiles can be removed, for example by heating and/or
33 subjecting the product to subatmospheric pressures.

1 A polymer polyol of the invention may contain 5 to 65%, preferably 15 to 55% and
2 more preferably 35 to 50%, by weight of dispersed polymer particles. In general, the
3 amount of dispersed polymer particles in the product is taken to be the same as the
4 amount of low molecular weight monomers used in the polymer polyol production
5 process. The size of the dispersed thermoplastic polymer particles may be from about
6 100 nanometers to 100 microns in diameter, as measured by microscopy, with a
7 preferred minimum particle size being at least 250 nanometers, a preferred maximum
8 particle size being 20 microns, and a more preferred particle size being from 250
9 nanometers to 20 microns and an especially preferred particle size being from 500
10 nanometers to 3 microns. An advantage of this invention is that somewhat larger
11 amounts of stabilizer can be used in this invention without leading to a large increase in
12 viscosity when water is added to the product. Because larger amounts of stabilizer can
13 be used, better stabilization of the monomer droplets is seen, which leads to smaller
14 particle sizes. Smaller particle size may relate to improvements in reinforcing efficiency
15 (as manifested by foam hardness normalized to density) that are often seen when the
16 polymer polyol of the invention is used to manufacture flexible polyurethane foam.

17 The macromer and/or pre-formed polymer of the macromer (which may be
18 grafted to the dispersed polymer particles) may constitute 0.25 to 10%, preferably from
19 0.5 to 8% and more preferably from 0.5 to 5% based on the weight of the product. The
20 polyol(s) that form the continuous polyol phase may constitute 10 to 94%, preferably 30
21 to 70%, more preferably 40 to 60% by weight, based on the weight of the product.

22 The polymer polyol is useful to make a wide variety of polyurethane and/or
23 polyurea products. The polyurethane and/or polyurea products will be in most instances
24 elastomeric materials that may be non-cellular, microcellular or foamed. Polyurethanes
25 are typically prepared by reacting the polymer polyol or dispersion with a
26 polyisocyanate. The polymer polyol product may be blended with one or more additional
27 polyols, including those types described above, to adjust the solids content to a desired
28 level or provide particular characteristics to a polyurethane made from the polymer
29 polyol. The reaction with the polyisocyanate is performed in the presence of a blowing
30 agent or gas when a cellular product is desired. The reaction may be performed in a
31 closed mold, but in some applications, such as slabstock foam, the reaction mixture is
32 generally permitted to rise more or less freely to form a low density foam material.
33 Generally, the polymer polyol of the invention can be used in the same manner as

1 conventional polymer polyol materials, using the same general types of processes as are
2 used with the conventional materials.

3 Suitable polyisocyanates include aromatic, cycloaliphatic and aliphatic
4 isocyanate. Exemplary polyisocyanates include m-phenylene diisocyanate, toluene-2,4-
5 diisocyanate, toluene-2,6-diisocyanate, hexamethylene-1,6-diisocyanate,
6 tetramethylene-1,4-diisocyanate, cyclohexane-1,4-diisocyanate, hexahydrotoluene
7 diisocyanate, naphthylene-1,5-diisocyanate, 1,3- and/or 1,4-
8 bis(isocyanatomethyl)cyclohexane (including cis- and/or trans isomers) methoxyphenyl-
9 2,4-diisocyanate, diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-
10 diisocyanate, hydrogenated diphenylmethane-4,4'-diisocyanate, hydrogenated
11 diphenylmethane-2,4'-diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dimethoxy-4,4'-
12 biphenyl diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 3,3'-dimethyldiphenyl
13 methane-4,4'-diisocyanate, 4,4',4"-triphenyl methane triisocyanate, a polymethylene
14 polyphenylisocyanate (PMDI), toluene-2,4,6-triisocyanate and 4,4'-
15 dimethyldiphenylmethane-2,2',5,5'-tetraisocyanate. Preferably the polyisocyanate is
16 diphenylmethane-4,4'-diisocyanate, diphenylmethane-2,4'-diisocyanate, PMDI, toluene-
17 2,4-diisocyanate, toluene-2,6-diisocyanate or mixtures thereof. Diphenylmethane-4,4'-
18 diisocyanate, diphenylmethane-2,4'-diisocyanate and mixtures thereof are generically
19 referred to as MDI, and all can be used. Toluene-2,4-diisocyanate, toluene-2,6-
20 diisocyanate and mixtures thereof are generically referred to as TDI, and all can be
21 used.

22 The amount of polyisocyanate used in making a polyurethane is commonly
23 expressed in terms of isocyanate index, *i.e.*, 100 times the ratio of NCO groups to
24 isocyanate-reactive groups in the reaction mixture (including those provided by water if
25 used as a blowing agent). In general, the isocyanate index may range as low as 60 and
26 as high as 500 or more. However, for the production of conventional slabstock foam, the
27 isocyanate index typically ranges from about 95 to 140, especially from about 105 to 115.
28 In molded and high resiliency slabstock foam, the isocyanate index typically ranges from
29 about 50 to about 150, especially from about 85 to about 110.

30 A catalyst is often used to promote the polyurethane-forming reaction. The
31 selection of a particular catalyst package may vary somewhat with the particular
32 application, the particular polymer polyol or dispersion that is used, and the other
33 ingredients in the formulation. The catalyst may catalyze the "gelling" reaction between

1 the polyol(s) and the polyisocyanate and/or, in many polyurethane foam formulation(s),
2 the water/polyisocyanate ("blowing") reaction which generates urea linkages and free
3 carbon dioxide to expand the foam. In making water-blown foams, it is typical to use a
4 mixture of at least one catalyst that favors the blowing reaction and at least one other
5 that favors the gelling reaction.

6 A wide variety of materials are known to catalyze polyurethane-forming
7 reactions, including tertiary amines, tertiary phosphines, various metal chelates, acid
8 metal salts, strong bases, various metal alcoholates and phenolates and metal salts of
9 organic acids. Catalysts of most importance are tertiary amine catalysts and organotin
10 catalysts. Examples of tertiary amine catalysts include: trimethylamine, triethylamine,
11 N-methylmorpholine, N-ethylmorpholine, N,N-dimethylbenzylamine, N,N-
12 dimethylethanolamine, N,N,N',N'-tetramethyl-1,4-butanediamine, N,N-
13 dimethylpiperazine, 1,4-diazobicyclo-2,2,2-octane, bis(dimethylaminoethyl)ether,
14 triethylenediamine and dimethylalkylamines where the alkyl group contains from 4 to
15 18 carbon atoms. Mixtures of these tertiary amine catalysts are often used.

16 Examples of organotin catalysts are stannic chloride, stannous chloride, stannous
17 octoate, stannous oleate, dimethyltin dilaurate, dibutyltin dilaurate, other organotin
18 compounds of the formula $\text{SnR}_n(\text{OR})_{4-n}$, wherein R is alkyl or aryl and n is 0-2, and the
19 like. Commercially available organotin catalysts of interest include Dabco™ T-9 and T-
20 12 catalysts (both stannous octoate compositions available from Evonik Corporation).

21 Catalysts are typically used in small amounts, for example, each catalyst being
22 employed from about 0.0015 to about 5% by weight of the high equivalent weight polyol.

23 When forming a foam, the reaction of the polyisocyanate and the polyol
24 component is conducted in the presence of a blowing agent. Suitable blowing agents
25 include physical blowing agents such as various low-boiling chlorofluorocarbons,
26 fluorocarbons, hydrocarbons and the like. Fluorocarbons and hydrocarbons having low
27 or zero global warming and ozone-depletion potentials are preferred among the physical
28 blowing agents. Chemical blowing agents that decompose or react to produce a gas
29 under the conditions of the polyurethane-forming reaction are also useful.

30 The blowing agent may be, for example, water or a mixture of water and a
31 physical blowing agent such as a fluorocarbon, hydrofluorocarbon, hydrochlorocarbon or
32 hydrocarbon blowing agent. Water reacts with isocyanate groups to liberate carbon
33 dioxide and form urea linkages. Typically, about 1 to about 7, especially from about 2.5

1 to about 5, parts by weight water are typically used per 100 parts by weight of polyols in
2 the foam formulation.

3 Alternatively or in addition, a gas such as carbon dioxide, air, nitrogen or argon
4 may be used as the blowing agent to produce polyurethane foam in a frothing process.
5 Carbon dioxide can also be used as a liquid or as a supercritical fluid.

6 A foam-stabilizing surfactant is also used when a polyurethane foam is prepared.
7 A wide variety of silicone surfactants as are commonly used in making polyurethane
8 foams can be used in making the foams with the polymer polyols or dispersions of this
9 invention. Examples of such silicone surfactants are commercially available under the
10 tradenames Tegostab™ (Evonkic Corporation), Niox™ (Momentive Performance
11 Materials) and Dabco™ (Evonik Corporation).

12 In addition to the foregoing components, the polyurethane formulation may
13 contain various other optional ingredients such as cell openers; fillers such as calcium
14 carbonate; pigments and/or colorants such as titanium dioxide, iron oxide, chromium
15 oxide, azo/diazo dyes, phthalocyanines, dioxazines and carbon black; reinforcing agents
16 such as fiber glass, carbon fibers, flaked glass, mica, talc and the like; biocides;
17 preservatives; antioxidants; flame retardants; and the like.

18 In general, a polyurethane foam is prepared by mixing the polyisocyanate and
19 polymer polyol in the presence of the blowing agent, surfactant, catalyst(s) and other
20 optional ingredients as desired, under conditions such that the polyisocyanate and
21 polyol react to form a polyurethane and/or polyurea polymer while the blowing agent
22 generates a gas that expands the reacting mixture. The foam may be formed by the so-
23 called prepolymer method (as described in U.S. Pat. No. 4,390,645, for example), in
24 which a stoichiometric excess of the polyisocyanate is first reacted with the high
25 equivalent weight polyol(s) to form a prepolymer, which is in a second step reacted with
26 a chain extender and/or water to form the desired foam. Frothing methods (as described
27 in U.S. Pat. Nos. 3,755,212; 3,849,156 and 3,821,130, for example), are also suitable. So-
28 called one-shot methods (such as described in U.S. Pat. No. 2,866,744) are preferred. In
29 such one-shot methods, the polyisocyanate and all polyisocyanate-reactive components
30 are simultaneously brought together and caused to react. Three widely used one-shot
31 methods which are suitable for use in this invention include slabstock flexible foam
32 processes, high resiliency flexible slabstock foam processes, and molded flexible foam
33 methods.

1 The following examples are provided to illustrate the invention, but are not
2 intended to limit the scope thereof. All parts and percentages are by weight unless
3 otherwise indicated.

4 5 **Examples**

6 Vinyl benzyl glycidyl ether (VBGE) is synthesized as follows: 4-vinylphenyl
7 methanol (98.3 parts), epichlorohydrin (106.2 parts), triethyl amine (74.2 parts) and
8 NaOH (29.3) parts are mixed in a flask in an ice bath and stirred overnight. The
9 resulting product is filtered. The filtrate is stripped under vacuum to remove
10 triethylamine and then at 80°C and 10 millibars pressure until no further vapors
11 condense. The product vinyl benzyl glycidyl ether is confirmed by NMR and gas
12 chromatography.

13 100 parts of a nominally hexafunctional, 1864 equivalent weight random
14 copolymer of 88.5% propylene oxide and 11.5% ethylene oxide are combined with about
15 2000 ppm of potassium hydroxide. 0.7 parts of VBGE are added at room temperature
16 and the resulting reaction mixture is held at that temperature under a nitrogen
17 atmosphere for 24 hours. The product is filtered and t-butyl catechol is dissolved into it.
18 These amounts of VBGE and copolymer correspond to a mole ratio of approximately 0.41
19 moles of VBGE per mole of copolymer. About 87% of the VBGE reacts under these
20 conditions. The product is a mixture of macromer and unreacted copolymer, the
21 macromer constituting approximately 36% of the total weight of product. The macromer
22 molecules mostly have 6 hydroxyl groups and a single terminal carbon-carbon double
23 bond.

24 When a similar capping reaction is performed substituting isopropenylphenyl
25 glycidyl ether for the VBGE, only about 9% of the isopropenylphenyl glycidyl ether reacts
26 to form macromer, and various unwanted side-products form. When divinylbenzene
27 monoxide is substituted for the VBGE, only about 50% of the divinylbenzene monoxide
28 reacts.

29 Polymer polyol Example 1 is prepared by charging a stirred reactor with a
30 mixture of 58.1 parts of a base polyol (a 1000 hydroxyl equivalent weight, nominally
31 trifunctional random copolymer of 88.5% propylene oxide and 11.5% ethylene oxide), 2.5
32 parts of a previous-formed polymer polyol (the heel of a previous polymerization
33 reaction) and 5.0 parts of the mixture of macromer and unreacted copolymer from above

1 (i.e., about 1.8 parts of the macromer). This mixture is purged with nitrogen and
2 vacuum several times. The internal reactor pressure is brought to 10 kPa and the
3 mixture is then heated to 125°C. Separately, 70 parts of styrene, 30 parts of
4 acrylonitrile, 0.49 parts of n-dodecylmercaptan and 0.18 parts of a free radical initiator
5 are homogenized in a small amount of the base polyol. This blend is added to the stirred
6 reactor at a uniform rate over three hours. At the end of the monomer addition, a blend
7 of a second free radical initiator in a small amount of base polyol is added. The reaction
8 temperature is then increased by 5°C every 30 minutes until a temperature of 145°C is
9 attained, after which the reactor contents are allowed to react for another 60 minutes.
10 The reactor is then cooled to 40°C. The resulting product is stripped under vacuum.
11 This product, a stable, uniform dispersion of polymer particles in the base polyol, is
12 designated Example 1. It contains 34% by weight dispersed styrene-acrylonitrile
13 particles. The product is stable against settling and otherwise is similar in properties to
14 an otherwise like polymer polyol product made using a TMI-capped polyether as the
15 macromer.

16 Comparative Polymer Polyol A is made in the same general manner, increasing
17 the amounts of styrene and acrylonitrile to produce a 43% solids copolymer polyol
18 product. The stabilizer in this case is made by capping 100 parts by weight of the 1864
19 equivalent weight copolymer with 0.9 parts of TMI (3-isopropenyl- α,α -
20 dimethylbenzylisocyanate). This results in a mixture containing about 45% capped
21 copolymer and 55% of the 1864 equivalent weight copolymer.

22 Comparative Polymer Polyol B is made using the same ingredients as
23 Comparative Polymer Polyol A, except in a continuous process. The polymer polyol has
24 made has 44% solids.

25 The particles of Polymer Polyol Example 1 are similarly sized to those of
26 Comparative Samples A and B, with essentially all particles having a size of less than
27 10 μm as measured by laser diffraction methods.

28 Flexible polyurethane foams are made from each of Polymer Polyol Example 1
29 and Comparative Polymer Polyols A and B. The formulations are as set forth in Table
30 1. The various ingredients are separately weighed out into suitably sized vessels.
31 Polyol A (a 3500 molecular weight, nominally trifunctional random copolymer of
32 propylene oxide and ethylene oxide), the polymer polyol, silicone surfactant, water and
33 amine catalysts are combined in a flask using a high speed mixer at $23\pm 3^\circ\text{C}$. A greater

amount of Polyol A is added in Comparative Samples F-A through F-D to dilute the formulations to equivalent levels of styrene-acrylonitrile particles. Stannous octoate is added after 30 seconds, followed 10 seconds later by the polyisocyanate. The reaction mixture is mixed for an additional 10 seconds and then poured into an open 8 liter box, where it rises. 320 seconds after the polyisocyanate (80/20 mixture of 2,4- and 2,6-toluene diisocyanate) is added, the foams are transferred to a 140°C oven for 5 minutes to complete the cure. The foams are then aged for 24 hours at 23±3°C for 24 hours before samples are taken for property testing.

The foams are evaluated for density (ISO 845), compression force deflection (CFD) (ISO 3386-1), tensile and elongation (ISO1798), tear strength (ISO 8067) resilience (ASTM D3574), airflow (ISO7231), compression set (ISO 1856) and wet compression set (ISO 13362). Results are as indicated in Table 2.

Table 1

Ingredient	Parts by Weight					
	Ex. 1	F-A*	F-B*	Ex. 2	F-C*	F-D*
Polyol A	70.4	76.7	77.3	70.4	76.7	77.3
Polymer Polyol Ex. 1	29.6	0	0	29.6	0	0
Polymer Polyol A	0	23.3	0	0	23.3	0
Polymer Polyol B	0	0	22.7	0	0	22.7
Amine Catalysts ¹	0.16	0.16	0.16	0.10	0.10	0.10
Silicone Surfactant ²	0.8	0.8	0.8	0.5	0.5	0.5
Stannous Octoate	0.18	0.18	0.18	0.15	0.15	0.15
Water	3.9	3.9	3.9	2.2	2.2	2.2
TDI (index)	110	110	110	110	110	110

***Not an example of the invention.** ¹A mixture of bis(dimethylaminoethyl)ether and triethylendiamine. ²Niax L580, from Momentive Performance Materials.

Table 2

Property	Result					
	Ex. 1	F-A*	F-B*	Ex. 2	F-C*	F-D*
Density, kg/m ³	27.5	27.25	26.9	41.7	41.6	41.5
CFD (40%), kPa	5.2	5.2	5.8	5.5	5.5	5.8
CFD Sag factor	2.6	2.5	2.5	2.5	2.5	2.5
CFD Hysteresis, %	57.8	56.8	56.7	73.7	73.8	73.5
Tensile Str., kPa	133	129	131	147	135	141
Elongation, %	147	148	130	151	147	136
Tear Str., N/m	385	425	357	371	378	486
Resilience, %	35.8	31.3	30.3	42.0	41.3	41.0
75% Compression Set, %	12	19	11	5	6	5
90% Compression Set, %	23	18	17	11	12	11
Wet Compression Set, %	14	16	10	4	4	4

***Not an example of the invention.**

As the foregoing data shows, the macromer made using VBGE produces a polyurethane foam having properties that are not meaningfully different from those produced using a TMI-capped macromer.