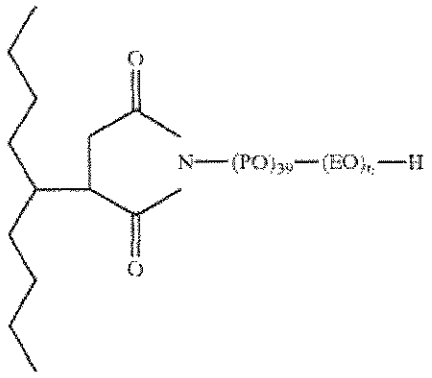
Since there is no opportunity for polymerization in the mechanical dispersion process, the stabilizers in this case have been of the polymeric type. USP 6,613,827 describes a stabilizer made in the reaction of a monoamine polyol with a maleic anhydride functionalized polyethylene wax. The structure of this stabilizer is given as:



WO 2009/155427 describes stabilizers which are a copolymer of (1) from 10 to 70% by weight of a branched polyol which has a molecular weight from 4000 to 20,000, from 0.2 to about 1.2 polymerizable ethylenically unsaturated groups per molecule and from about 3 to about 8 hydroxyl groups per molecule with (2) from 30 to 90% by weight of styrene or a mixture of styrene and one or more other low molecular weight monomers. The copolymeric stabilizers are made in a free-radical polymerization process. These stabilizers theoretically have structures as depicted by Figure 1, but in reality the stabilizers obtained this way have large variability in their structures, and contain large fractions of polymers that do not have pendant polyether groups. The polymers lacking pendant polyether groups are ineffective as dispersion stabilizers.

What is desired is a stabilizer that more effectively stabilizes a dispersion of polymer particles in a polyether phase, to produce a low viscosity product having small dispersed particles. It is especially desirable that the stabilizer works well in a mechanical dispersion process to produce a dispersion having good stability, a small particle size and a low product viscosity.

T~~In one aspect, t~~his ~~invention~~disclosure is a process for making a polymer polyol, comprising forming a dispersion of solid polymer particles in the presence of a continuous liquid polyol phase and a stabilizer copolymer produced by copolymerizing an unsaturated polyether which has a molecular weight from 2000 to 20,000 and from 0.2 to about 1 polymerizable unsaturated groups per molecule with one or more copolymerizable low molecular weight unsaturated monomers in a controlled radical polymerization to form

a stabilizer copolymer having a number average molecular weight from 30,000 to 500,000 and an average of 1 to 20 pendant polyether chains per molecule.

In one aspect, there is provided a process for making a polymer polyol, comprising forming a dispersion of solid polymer particles in the presence of a continuous liquid polyol phase and a stabilizer copolymer produced by copolymerizing a linear unsaturated polyether which has a molecular weight from 2000 to 20,000 and from 0.2 to 1 polymerizable unsaturated groups per molecule with styrene or a mixture of styrene and one or more of acrylonitrile, butadiene, methyl methacrylate, butyl acrylate and vinyl acetate in a nitroxide-mediated polymerization in the presence of TEMPO or SG1 as a nitroxide radical or MAMA-SG1 as an alkoxyamino source for a nitroxide radical, or reversible addition-fragmentation chemical transfer (RAFT) polymerization in the presence of S-1-dodecyl-S'-(α,α'-dimethyl-a"-acetic acid)trithiocarbonate as the RAFT initiator to form a stabilizer polymer or copolymer having a number average molecular weight from 30,000 to 500,000 and an average of 1 to 20 pendant polyether chains per molecule, wherein the solid polymer particles are polystyrene or a copolymer of one or more of acrylonitrile, butadiene, methyl methacrylate, butyl acrylate and vinyl acetate.

In this process, the stabilizer polymer or copolymer facilitates the production of polymer polyol products having low viscosities and desirably small dispersed phase particles. The excellent results obtained from this process are believed to be due in part to the lower polydispersities and relatively homogeneous compositions of the stabilizers, compared to previous stabilizers made in a conventional free radical process, with fewer polymeric materials being formed that are devoid of pendant polyether chains.

The stabilizer copolymers produced in the controlled radical mediation polymerization can have various structures, including a star-grafted copolymer structure such as shown in Figure 1 or a "comb" structure as shown in Figure 2. In preferred embodiments, the stabilizer has a "toothbrush" structure as shown in Figure 3 or a "palm tree" structure as shown in Figure 4. A stabilizer having a toothbrush or palm-tree structure is a block copolymer that includes a first block having a molecular weight of at least 18,000, and preferably up to 400,000, that is devoid of pendant polyether groups. The block copolymer also includes a second block which is a homopolymer of an unsaturated polyether which has a molecular weight from 2000 to 20,000 and from 0.2 to about 1.0 polymerizable unsaturated groups per molecule or a

copolymer of said unsaturated polyether with one or more copolymerizable low molecular weight unsaturated monomers. The second block contains from 2 to 20 pendant polyether groups that each has a molecular weight from 2000 to 20,000.

In some embodiments, the dispersion is formed in a melt dispersion process which includes the steps of (a) mixing a melted thermoplastic polymer with the liquid polyol in the presence of the stabilizer under conditions sufficient to disperse the melted thermoplastic polymer in the form of droplets within a continuous phase of the liquid polyol and (b) cooling the dispersed polymer droplets in the polyol to solidify the polymer droplets and form the polymer polyol. In other embodiments, the dispersion is formed in an *in situ* polymerization process which includes the steps of polymerizing one or more low molecular weight monomers in the presence of the continuous polyol phase and the stabilizer under conditions such that the low molecular weight monomer(s) polymerize to form polymer particles dispersed in the continuous polyol phase.

In some embodiments, the ~~invention~~disclosure is a process for making a polymer polyol comprising forming a dispersion of solid polymer particles in the presence of a continuous liquid polyol phase and a stabilizer block copolymer having a first block

having a molecular weight of at least 18,000 and which is devoid of pendant polyether groups and a second block which is a homopolymer of a branched or linear unsaturated polyether which has a molecular weight from 2000 to 20,000 and from 0.2 to about 1 polymerizable unsaturated group per molecule or a copolymer of said unsaturated polyether with one or more copolymerizable low molecular weight unsaturated monomers, the second block containing from 2 to 20 pendant branched or linear polyether groups that each have a molecular weight from 2000 to 20,000.

In another aspect, there is provided a process for making a polymer polyol comprising forming a dispersion of solid polymer particles in the presence of a continuous liquid polyol phase and a stabilizer block copolymer having a first block formed in a first polymerization step in which styrene or a mixture of styrene and one or more of acrylonitrile, butadiene, methyl methacrylate, butyl acrylate and vinyl acetate are polymerized in a controlled radical polymerization in the absence of an unsaturated polyether to produce a living macroinitiator, wherein the controlled radical polymerization is a nitroxide-mediated polymerization in the presence of TEMPO or SG1 as a nitroxide radical or MAMA-SG1 as an alkoxyamine source for a nitroxide radical or reversible addition-fragmentation chemical transfer (RAFT) polymerization in the presence of S-1-dodecyl-S'-(α,α'-dimethyl-a"-acetic acid)trithiocarbonate) as the RAFT initiator, the first block having a molecular weight of at least 18,000 and being devoid of pendant polyether groups and a second block which is a homopolymer of a linear unsaturated polyether which has a molecular weight from 2000 to 20,000 and from 0.2 to 1 polymerizable unsaturated group per molecule or a copolymer of said unsaturated polyether with one or more copolymerizable unsaturated monomers, having a molecular weight no greater than 500, the second block being formed by copolymerizing an unsaturated polyether with one or more monomers, having a molecular weight no greater than 500, in the presence of the living macroinitiator and containing from 2 to 20 pendant branched or linear polyether groups that each have a molecular weight from 2000 to 20,000, wherein the solid copolymer particles are polystyrene or a copolymer of one or more of acrylonitrile, butadiene, methyl methacrylate, butyl acrylate and vinyl acetate.

The ~~invention~~disclosure is also a polymer polyol comprising a continuous polyol phase, a disperse phase of polymer particles and a stabilizer copolymer, which polymer polyol is produced in accordance with any of the foregoing aspects or embodiments of the ~~invention~~disclosure.

In another aspect, there is provided a polymer polyol formed in the process as disclosed above.

Figure 1 is a representation of the structure of a "star-grafted" stabilizer.

Figure 2 is a representation of the structure of a "comb" stabilizer.

Figure 3 is a representation of the structure of a "toothbrush" stabilizer.

Figure 4 is a representation of the structure of a "palm tree" stabilizer.

The stabilizer is a copolymer of an unsaturated polyether with one or more low molecular weight monomers. The unsaturated polyether is characterized in having a molecular weight from 2000 to 12,000, preferably at least 4000. Polyether molecular weights are conveniently determined by end-group analysis methods such as ATDM D4274-11. This polyether contains at least 1, preferably up to about 8, hydroxyl groups per molecule and at least one polymerizable unsaturated group per molecule. The unsaturated polyether preferably does not contain, on average, more than 1 polymerizable unsaturated group per molecule. By "unsaturated group", it is meant a carbon-carbon double or triple bond, such as a vinyl or substituted vinyl group.

The unsaturated polyether can be prepared in either of two main methods. One method can be generally described as forming a linear or branched polyether having a molecular weight from 2000 to 20,000 and from 1 to 9, preferably from 2 to 9, hydroxyl groups per molecule, and "capping" one or more of the hydroxyl groups with an unsaturated capping agent. The capping agent includes, in addition to the polymerizable unsaturation, a functional group that can react with a hydroxyl group of the polyether (or a corresponding alkoxide ion) to form a covalent bond to the polyether. The capping agent may be, for example, an ethylenically unsaturated isocyanate compound such as 3-isopropenyl-α,α-dimethylbenzylisocyanate (TMI) or isocyanatoethylmethacrylate (IEM), an ethylenically unsaturated halide such as vinyl