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# (54) Title: METHOD OF REDUCING MOLECULAR WEIGHTS AND POLYDISPERSITY INDICES OF POLYMERS OF ETHYLENE OXIDE

## (57) Abstract

A method for reducing the molecular weights of polymers is disclosed. The method of the invention can also be used as a method of reducing the polydispersity index of a polymer, particularly commercially available, low molecular weight grades of poly(ethylene oxide). The method comprises adding on initiator to a polymer and heating and mixing the polymer and the initiator. Optionally, a monomer such as 2–ethylhexyl methacrylate, 2–hydroxyethyl methacrylate or polylethylene glycol) methacrylate is added to the mixture to promote grafting and lessen cross–linking. The method produces a polymer with a reduced molecular weight and, optionally, a reduced polydispersity index. The method is particularly useful for reducing the molecular weights and polydispersity indices of polymers of ethylene oxide. The method of the invention can be used to pelletize high molecular weight grades of poly(ethylene oxide) without the addition of plasticizers.

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# METHOD OF REDUCING MOLECULAR WEIGHTS AND POLYDISPERSITY INDICES OF POLYMERS OF ETHYLENE OXIDE

## CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims priority to U.S. provisional patent application Serial No. 60/070,140 entitled "Method of Reducing the Molecular Weights and Polydispersity Index of Poly(ethylene oxide)" filed December 31, 1997.

## FIELD OF THE INVENTION

The present invention is directed to a method of reducing the molecular weight of a polymer. The method is also capable of decreasing the polydispersity indices of polymers. The method is particularly useful for reducing the molecular weight of polymers of ethylene oxide. Optionally, the method may be used to reduce the polydispersity index of a polymer of ethylene oxide that is the product of the degradation of a higher molecular weight polymer. The method of reducing the molecular weight of a polymer is achieved by adding an initiator to a reaction mixture comprising the polymer and heating the reaction mixture.

## BACKGROUND OF THE INVENTION

Synthetic polymer compositions are composed of many polymer molecules having various chain lengths and molecular weights. That is, a synthetic polymer composition is composed of polymer molecules of differing chain lengths and molecular weights as opposed to being composed of molecules of the exact same length and molecular weight. The differing lengths and molecular weights of the polymer molecules within the polymer composition result from the kinetics of the particular polymerization process used to produce the polymer. Thus, a polymer composition has a distribution of molecular weights.

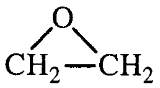
Many commercially available polymers have broad molecular weight distributions. The breadth of the molecular weight distribution of a polymer can be measured by the polydispersity index ($M_w/M_n$) of the polymer. The polydispersity index is the ratio of the weight-average molecular weight ($M_w$) of the polymer to the number-average molecular weight ($M_n$) of the polymer. The weight-average molecular weight and the number-average molecular weight of a polymer can be determined by analytical methods, such as gel permeation chromatography. Once the weight-average and number-average molecular weights have been determined, the polydispersity index is easily calculated by dividing the weight-average molecular weight by the number average molecular weight, $M_w/M_n$. A hypothetically monodisperse polymer has a polydispersity index of 1.000. However, typical commercial polymers, such as the commercially available poly(ethylene oxide) resins discussed herein, have a polydispersity index of 10 or more. Polymers with broad molecular weight distributions have higher polydispersity indices and polymers with narrow molecular weight distributions have lower polydispersity indices.

High molecular weight polymers usually have poor processability for manufacturing into films and fibers. High molecular weight polymers also have high melt viscosities, high melt pressures and increase melt degradation resulting from increased shear heating versus lower molecular weight polymers. Typically, polymers having narrow molecular weight distributions, and correspondingly low polydispersity indices, have desirable properties and are easily and more processable compared to the same polymer with a broader molecular weight distribution and correspondingly higher polydispersity indices. Therefore, it would be desirable to develop a method of reducing the polydispersity index of a polymer.

Poly(ethylene oxide) is a homopolymer of ethylene oxide, that is represented by the formula

$$-(CH_2CH_2O)_n-$$

and is produced from the ring opening polymerization of the ethylene oxide,



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Typically, polyethylene oxide (hereinafter PEO) resins are available in only broad molecular weight distributions and correspondingly high polydispersity indices. These PEO resins are difficult to process and possess undesirable properties.

PEO is typically produced at an average molecular weight of about 4,000,000 gram per mole (hereinafter g/mol). Lower molecular weight grades of PEO resins are produced by degrading 4,000,000 g/mol average molecular weight PEO resins with a radiation source. This process produces PEO compositions with broad molecular weight distributions and high polydispersity indices. Because of the kinetics of the polymerization process used to produce PEO, commercially available PEO resins are produced having polydispersity indices greater than about 12. Examples of currently available PEO resins include POLYOX® WSR N-80, WSR 12K, and WSR 205 PEO resins, which are commercially available from Union Carbide. These PEO resins have polydispersity indices that range from about 12 to 20 and are not easily melt processed. These highly dispersed PEO resins include a high molecular weight fraction contained in the broad molecular weight distribution that brings about the poor melt processability.

One method of reducing the molecular weight of PEO is described in U.S. Patent No. 4,200,704. U.S. Patent No. 4,200,704 describes a method that is carried out in a partial pressure of oxygen in an inert atmosphere in order to avoid potential explosive conditions. The method requires the suspension of the PEO in a solvent. The use of solvents is undesirable both economically and environmentally. Further, most of the solvents employed are flammable. It is desirable to develop a method of producing low molecular weight PEO resins that does not require the use of solvents.

Another method of reducing the molecular weight of PEO is discussed in the background U.S. Patent No. 4,200,704. This other method uses a radiation source, such as cobalt-60, to degrade the PEO to lower molecular weights. Radiation degradation has limitations including nonuniformity of the resulting, degraded resin polymer as demonstrated by the high polydispersity indices of the resulting, degraded resins. Commercial grades of PEO having average molecular weights of about 400,000 g/mol and greater that are produced by irradiation degradation require plasticizers in order to improve their processabilities to within useful limits. In the presence of plasticizers, these PEO resins, such as commercial POLYOX® WSR 205 and WSR N-12K PEO resin of 600,000 and 1,000,000 g/mol average molecular weight, still have poor melt processability and exhibit extreme melt fracture during conventional melt processing. The poor melt processabilities of these PEO resins leads to the conclusion that conventional PEO resins cannot be fabricated into films of

1 mil or less in thickness using conventional melt processing techniques. For example, the thickness of the thinnest films that can be melt fabricated from conventional PEO resins having average molecular weights of 400,000 g/mol or greater is not less than about 7 mils. Additionally, the use of radiation to lower the molecular weight of polymer resins is dangerous and environmentally undesirable.

The PEO resins produced by the irradiation method are supplied as a fine powder and cannot be easily melt processed in conventional thermoplastic extrusion apparatus for film and fiber manufacturing due to the inherent difficulties of working with fine powders. These difficulties are due to the fine size of the PEO particles, the low melting point of the particles and the agglomeration of the particles in the feeding section of the processing apparatus. Additionally, PEO powder cannot be shipped in bulk due to explosion hazards. PEO resins must be shipped in drums, which adds to the cost of the PEO resin. Thus, it would also be desirable to provide a method of pelletizing PEO resins so that they can be easily and economically shipped in bulk.

Both of these methods of reducing or modifying the molecular weights of PEO require additional steps, are costly, hazardous and inefficient and produce PEO of broad molecular weight distributions. It would be desirable to develop a method of reducing the molecular weight of PEO and other polymers that does not require the use of a diluent or a radiation source and that overcomes the disadvantages of the prior art. Although, the method of U.S. Patent No. 4,200,704 and irradiation with a radioactive source produce PEO of lower molecular weights, the methods produce PEO resins with broad molecular weight distributions and correspondingly high polydispersity indices and results in PEO resins that are undesirable for processing. Therefore, it would also be desirable to develop a method of reducing the molecular weight of PEO that produces low molecular weight PEO with a low polydispersity index and correspondingly narrow molecular weight distribution having more improved processing properties.

## SUMMARY OF THE INVENTION

The present invention is directed to methods for reducing the molecular weights and polydispersity indices of polymers. More particularly, the present invention relates to a method of reducing the molecular weight and polydispersity index of a polymer by heating the polymer and adding and mixing an initiator with the polymer. In one embodiment, the method comprises a method of reducing the polydispersity index and molecular weight of a polymer of ethylene oxide. Polymers whose molecular weights and/or polydispersity indices are reduced by the method of the present invention have improved melt processability and operating safety as indicated by the reduced torque, melt temperature and pressure measured during processing of the polymers.

In one embodiment of the present invention, the polymer is a polymer of ethylene oxide, specifically poly(ethylene oxide). However, the method of the invention includes both homopolymers and copolymers of ethylene oxide such as copolymers of ethylene oxide and other alkylene oxides. The method of the invention is particularly useful for reducing the molecular weight of the above polymers, whose initial molecular weight, i.e. before reactive extrusion, is in the range of from about 100,000 grams/mol to about 8,000,000 g/mol. The method is also useful for reducing the polydispersity index of polymers of ethylene oxide, particularly polymers of ethylene oxide, whose initial molecular weight is in the range of from about 100,000 grams/mol to about 2,000,000 g/mol. These lower molecular weight polymers of ethylene oxide are currently produced by irradiation and are not amenable to melt processing. The methods of molecular weight reduction and polydispersity index reduction include a free radical initiated degradation process of PEO by reacting PEO and a free radical under conditions sufficient to decompose the free radical initiator. Desirably, the method includes shear mixing of the PEO and the decomposed initiator to degrade the PEO.

Additionally, a monomer may be added to the reactive mixture during the process. Desirable monomers that are added during the process include both polar vinyl monomer, non-polar vinyl monomers, and mixtures thereof. Desirable polar monomers include, but are not limited to, acrylic acid, methacrylic acid, 2-hydroxyethyl methacrylate, poly(ethylene glycol) methacrylate and maleic anhydride. Desirable non-polar monomers include, but are not limited to, 2-ethylhexyl methacrylate, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate and their analogs, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate and their analogs, poly(ethylene glycol) phenyl ether acrylate and poly(ethylene glycol) alkyl ether methacrylates. The monomer or mixture of monomers may be added to the reactive mixture with or separately from, the initiator during the molecular weight reduction process. The mixture of monomers may include both polar and non-polar monomers in ratios ranging from 1:99 to 99:1 of polar to non-polar monomer. Although desirable, the addition of the monomer to the mixture of the polymer and the initiator is optional. The addition of the monomer results in grafting of the monomer onto the polymer.

The polymer, initiator and optional monomer may be added to the mixture simultaneously. It is desirable to add the polymer to the reactive vessel first. It is more desirable to add and disperse the monomer in the molten polymer before adding the initiator. Alternatively, the monomer may be added after the initiator and the molten polymer are combined.

In contrast to the prior art, the methods of the present invention do not require a solvent, an inert atmosphere, a particular oxygen concentration or a radiation source to reduce the molecular weight(s) or polydispersity index of a polymer. Additionally, the method of the present invention may be performed using conventional apparatuses and may be incorporated into conventional processes of forming articles from polymers, such as extrusion and injection molding. Thus, the method does not require additional processing steps or cost. The resulting polymers are useful in a broad range of thermoplastic operations including film and fiber forming, including non-woven processes such as spunbonding and meltblowing processes. Commercially available grades of poly(ethylene oxide) cannot be used in these applications due to inherent deficiencies in the melt properties of poly(ethylene oxide) except the very low molecular weight PEO resins, i.e. less than about 200,000 g/mol. Consequently, commercially available poly(ethylene oxide) are limited to solution applications.

Other features and advantages of the present invention will become apparent after a review of the following detailed description of the disclosed embodiments.

## DETAILED DESCRIPTION OF THE PRESENT INVENTION

The present invention is directed to a method of reducing the molecular weights of polymers. The method of the present invention produces improved, lower molecular weight polymer compositions and may be performed in one step using conventional apparatus. Beneficially, the method does not require the use of solvents, inert gasses, radiation sources or other hazardous conditions. When the method of the present invention is used on a polymer whose molecular weight has been previously reduced by irradiation, the resulting polymer has a molecular weight that is further reduced but also, surprisingly, has a reduced polydispersity index compared to the polymer prior to the present method. Irradiation reduced polymers include commercially available grades of poly(ethylene oxide) (hereinafter PEO) which are not melt processable. The modification of a PEO resin with the method of the present invention produces a PEO resin that is more easily processed by thermal processing techniques than the commercially available PEO resins from which the modified PEO was produced.

The method of the present invention is particularly useful for reducing the molecular weight of PEO, whose initial molecular weight, i.e. before reduction, is in the range of from about 100,000 grams/mol to about 8,000,000 g/mol. This range encompasses all PEO resins currently made by Union Carbide, the molecular weights of which were provided by Union Carbide as determined by rheological measurements. The molecular weights of these polymers as determined by gel permeation chromatography are also included in Table 2 below. The method is also useful for reducing the polydispersity index of PEO, whose initial molecular weight is in the range of from about 100,000 grams/mol to about 2,000,000 g/mol. Currently, lower molecular weight grades of PEO are produced by irradiation and are not amenable to melt processing. PEO resins produced in accordance with the present invention are amendable to melt processing and are useful in a broad range of applications, including extruding films and spinning fibers.

PEO resins useful for molecular weight reduction in accordance with the present invention may be obtained from various commercial suppliers, including Union Carbide Corporation. Various grades and weights of PEO resins are available from Union Carbide and are sold under the trade name and designations POLYOX® WSR N-10, WSR N-80, WSR N-750 WSR N-3000, WSR-3333, WSR 205, WSR N-

12K, WSR N-60K, WSR 301, WSR Coagulant and WSR 308. (See POLYOX®: Water Soluble Resins, Union Carbide Chemicals & Plastic Company, Inc., 1991 which is incorporated by reference herein in its entirety.) Both PEO powder and pellets of PEO may be used in the present invention because the physical form of PEO does not affect its behavior in the melt state. Commercially available PEO resins are supplied in powder form and cannot be directly used to make films due to feeding problems with PEO powder in the film making apparatus. Further, PEO powder cannot be shipped economically in railroad cars because of the explosive hazardous conditions created by loading and shipping PEO powder directly into railroad cars. PEO resins with molecular weights higher than 400,000 cannot be pelletized without the addition of a lubricant or plasticizer and PEO resins with molecular weights greater than 1,000,000 cannot be pelletized without melt fracture, even at low production rates and with high amounts of plasticizer. Further, the addition of plasticizer to PEO is only temporary and the plasticizer eventually migrates out of the PEO. This is a phenomenon known as blooming and results in a change in properties, most significantly, embrittlement. The present invention provides a method of pelletizing high molecular weight PEO. PEO resins modified in accordance with the present invention may be pelletized and melt extruded directly into films.

The prior art method of reducing the molecular weight of PEO described in U.S. Patent No. 4,200,704 requires the suspension of PEO particles in a solvent. The method of U.S. Patent No. 4,200,704 and the other prior art irradiation method discussed therein degrade only the surface of the PEO particles and produce lower weight PEO resins with broader molecular weight distributions. The present invention degrades the polymer in the melt state homogeneously in bulk, resulting in a lower molecular weight polymer with a more uniform, narrower molecular weight distribution. The present invention has been demonstrated by the use of PEO in powder form as supplied by Union Carbide and does not require the suspension of the PEO in a solvent. The PEO resin to be modified may be obtained from other suppliers and in other forms, including pellets containing plasticizers. The PEO resins and resulting modified compositions may optionally contain various additives such as plasticizers, processing aids, rheology modifiers, antioxidants, UV light stabilizers, pigments, colorants, slip additives, antiblock agents, etc., which may be added before or after modification.

A variety of free radical initiators may be useful in the practice of the present invention. In a reactive-extrusion process, it is desirable that the initiator generates free radicals through the application of heat. Such initiators are generally referred to as thermal initiators. For the initiator to function as a useful source of radicals, the initiator should be commercially and readily available, stable at ambient or refrigerated conditions, and generate radicals at reactive-extrusion temperatures. Desirably, the initiator should generate radicals at temperatures above the melting point of the polymer, whose molecular weight is to be reduced. In the following Examples, the reaction temperature is in the range from the melting point of the PEO to the decomposition temperature of the PEO. For PEO the desired range is from about 140°C to about 220°C. More desirably, the reaction temperature is within the range of from about 160°C to about 200°C. Desirably, the amount of initiator should be between about 0.05 to about 2 weight percent initiator relative to the weight of the polymer to be modified. More desirably, the amount of initiator should be between about 0.1 to about 1 weight percent initiator relative to the weight of the polymer to be modified. Even more desirably, the amount of initiator should be between about 0.1 to about 0.5 weight percent initiator relative to the weight of the polymer to be modified. A range of initiator levels is demonstrated in the following Examples.

Compounds containing an O-O, S-S, or N=N bond may be used as thermal initiators. Compounds containing O-O bonds, peroxides, are commonly used as initiators for polymerization and reactive-extrusion processes. Such commonly used peroxide initiators include, but are not limited to, alkyl, dialkyl, diaryl and arylalkyl peroxides such as cumyl peroxide, t-butyl peroxide, di-t-butyl peroxide, dicumyl peroxide, cumyl butyl peroxide, 1,1-di-t-butyl peroxy-3,5,5-trimethylcyclohexane, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexyne-3 and bis(a-t-butyl peroxyisopropylbenzene); acyl peroxides such as acetyl peroxides and benzoyl peroxides; hydroperoxides such as cumyl hydroperoxide, t-butyl hydroperoxide, p-methane hydroperoxide, pinane hydroperoxide and cumene hydroperoxide; peresters or peroxyesters such as t-butyl peroxypivalate, t-butyl peroctoate, t-butyl perbenzoate, 2,5-dimethylhexyl-2,5-di(perbenzoate) and t-butyl di(perphthalate); alkylsulfonyl peroxides; dialkyl peroxymonocarbonates; dialkyl peroxydicarbonates; diperoxyketals; ketone peroxides such as cyclohexanone peroxide and methyl ethyl ketone peroxide. Additionally, azo compounds such as 2,2'-azobisisobutyronitrile abbreviated as AIBN, 2,2'-azobis(2,4-dimethylpentanenitrile) and 1,1'-azobis(cyclohexanecarbonitrile) may be used as the initiator. The present invention has been demonstrated in the following Examples by the use of a liquid, organic peroxide initiator available from Elf Atochem North America, Inc. of Philadelphia, PA, sold under the trade designation LUPERSOL® 101 (hereinafter L101). LUPERSOL® 101 is a free radical initiator and comprises 2,5-dimethyl-2,5-di(t-butylperoxy) hexane. Other initiators and other grades of LUPERSOL® initiators may also be used, such as LUPERSOL® 130.

In a further embodiment of the present invention, one or more monomers may be added to the polymer/initiator mixture. The addition of monomers to the reaction mixture causes grafting of the monomer onto the polymer in addition to the degradation of the polymer. A variety of monomers may be useful in the practice of the present invention. Monomer(s) as used herein includes monomers, oligomers, polymers, mixtures of monomers, oligomers and/or polymers, and any other reactive chemical species, which is capable of covalent bonding with the parent polymer, such as PEO. Ethylenically unsaturated monomers containing polar or non-polar functional groups are appropriate for the present invention and are desired. Polar groups include, but are not limited to, hydroxyl, carboxyl, amino, carbonyl, halo, thiol, sulfonic, and sulfonate groups. Non-polar groups include, but are not limited to, alkyl, cycloalkyl, aromatic, benzylic, phenyl, and heterocyclical groups. Desirable ethylenically unsaturated monomers include acrylates and methacrylates. Desirable ethylenically unsaturated non-polar monomers include 2-ethylhexyl methacrylate (hereinafter “EHMA”), methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate, as well as their higher molecular weight analogs. Desirable ethylenically unsaturated polar monomers include 2-hydroxyethyl methacrylate (hereinafter “HEMA”); poly(ethylene glycol) methacrylates (hereinafter “PEG-MA”); poly(ethylene glycol) ethyl ether methacrylate; poly(ethylene glycol) acrylates; poly(ethylene glycol) ethyl ether acrylate; poly(ethylene glycol) methacrylates with terminal hydroxyl groups; acrylic acid; maleic anhydride; itaconic acid; sodium acrylate; 3-hydroxypropyl methacrylate; acrylamide; glycidyl methacrylate; 2-bromoethyl acrylate; carboxyethyl acrylate; methacrylic acid; 2-chloroacrylonitrile; 4-chlorophenyl acrylate; 2-cyanoethyl acrylate; glycidyl acrylate; 4-nitrophenyl acrylate;

pentabromophenyl acrylate; poly(propylene glycol) methacrylate; poly(propylene glycol) acrylate; 2-propene-1-sulfonic acid and its sodium salt; 2-sulfoethyl methacrylate; 3-sulfopropyl methacrylate; and 3-sulfopropyl acrylate. A particularly desired poly(ethylene glycol) methacrylate is poly(ethylene glycol) ethyl ether methacrylate. The term "poly(ethylene glycol) ethyl ether (meth)acrylate" as used herein includes both poly(ethylene glycol) ethyl ether methacrylate and poly(ethylene glycol) ethyl ether acrylate. The mixture of monomers may include both polar and non-polar monomers in ratios ranging from 1:99 to 99:1 of polar to non-polar monomer. It is expected that a wide range of polar and non-polar vinyl monomers would be capable of imparting similar effects as EHMA, HEMA or PEG-MA to a PEO resin and would be effective monomers for grafting.

As used herein, the term "graft copolymer" means a copolymer produced by the combination of two or more chains of constitutionally or configurationally different features, one of which serves as a backbone main chain, and at least one of which is bonded at some point(s) along the backbone and constitutes a side chain. As used herein, the term "grafting" means the forming of a polymer by the bonding of side chains or species at some point(s) along the backbone of a parent polymer. (See Sperling, L.H., Introduction to Physical Polymer Science 1986 pp. 44-47 which is incorporated by reference herein in its entirety.)

The amount of polar vinyl monomer relative to the amount of the present polymer may range from about 0.1 to about 20 weight percent of monomer to the weight of the present polymer. Desirably, the amount of monomer exceeds 0.1 weight percent in order to have a significant effect on the molecular weight and optionally the polydispersity of the parent polymer.

In one embodiment of the present invention, one or more vinyl monomers are grafted onto a parent polymer in a reactive extrusion process. The present invention is demonstrated in the Examples below by the use of PEO as the parent polymer. The incorporation of vinyl monomer into the PEO/initiator mixture improves the processability of the resulting polymer. The reactive extrusion of PEO with initiator alone produces two fractions of PEO: (1) a desired lower molecular weight fraction, which is thermoplastic and (2) an infinite molecular weight, crosslinked fraction, which is not thermoplastic. The crosslinked fraction is an insoluble and infusible, three-dimensional network of PEO that is not amenable to melt processing. The presence of the crosslinked PEO gel fraction renders the overall PEO composition undesirable for most thermoplastic applications because inclusion of particles of crosslinked PEO gel form defects in films, fibers and other products produced from the gel- containing PEO compositions. The addition of monomer significantly reduces and eliminates in most instances the proportion of crosslinked PEO by forming a graft copolymer of PEO instead of crosslinked PEO. For practical purposes, the amount of monomer may be at the lower end of the above-disclosed range in order to decrease costs. A range of grafting levels is demonstrated in the following Examples. Typically, the amount of monomer added is between about 1 percent and about 10 percent of the weight of the base PEO resin.

When PEO is the parent polymer, the presence of monomer(s) in the reaction system reduces or eliminates crosslinking, which is produced by the combination reaction that occurs between two PEO microradicals. As used herein, the term “microradicals” refers to polymer radicals generated by the attack of free radicals on a polymer chain. The inclusion of monomers in the reactive environment allows the microradicals to desirably react with the more reactive monomer species instead of another microradical. Thus, the possibility of gel formation may be significantly reduced by the inclusion of monomer allowing the manufacture of thermally processable PEO resins.

The present invention has been demonstrated in the following Examples by the use of EHMA, HEMA and PEG-MA as the monomer. The EHMA used in the Examples was supplied by Aldrich Chemical Company catalog number 29,080-7. The HEMA used in the Examples was supplied by Aldrich Chemical Company catalog number 12,863-5. And, the PEG-MA used in the Examples was supplied by Aldrich Chemical Company catalog number 40,954-5. This particular PEG-MA was a poly(ethylene glycol) ethyl ether methacrylate having a number average molecular weight of approximately 246 grams per mol. Poly(ethylene glycol) methacrylates with a number average molecular weight higher or lower than 246 g/mol are also applicable for the present invention. The molecular weight of the PEG-MA may range up to about 50,000 g/mol. However, lower molecular weights are desired for faster grafting reaction purposes. A desired range of the molecular weight of the monomer is from about 246 to about 5,000 g/mol and the most desired range is from about 246 to about 2,000 g/mol. Again, it is expected that a wide range of monomers, as well as, a wide range of molecular weights of monomers are capable of imparting similar effects to PEO resins and are effective monomers for grafting and molecular weight and polydispersity reduction purposes.

A variety of reaction vessels may be useful in the practice of the present invention. The modification of the polymer may be performed in any vessel as long as the necessary mixing and shearing of the polymer, the initiator and the optional monomer is achieved and enough thermal energy is provided to effect decomposition of the initiator, chain scission and, optionally, grafting. Desirably, such vessels include any suitable mixing device, such as continuous stir tank reactors, mixers, kneaders, extruders, including single and multiple screw extruders, and any other thermomechanical mixing devices, which may be used to mix, compound, process or fabricate polymers. In the following Examples, the reaction device is a twin-screw extruder, i.e. a ZSK-30 twin-screw extruder, manufactured by Werner & Pfleiderer Corporation of Ramsey, New Jersey. It should be noted that a variety of extruders may be used to modify polymers in accordance with the present invention provided that mixing and heating occur.

The ZSK-30 extruder has multiple ports, including venting ports, and is capable of processing polymers at a rate of up to 50 pounds per hour. If a higher rate of production is desired, an extruder of a larger diameter may be used. The ZSK-30 extruder has two modular screws and contains a variety of screw elements. The extruder may include conveying elements, kneading blocks or disks, left-handed screw elements, turbine mixing elements and other elements of various pitches and lengths. More particularly, the ZSK-30 extruder has a pair of co-rotating screws arranged in parallel with the center-to-center distance between the shafts of the two screws at 26.2 mm. The nominal screw diameters are 30 mm. The actual outer diameters of the screws are 30 mm and the inner screw diameters are 21.3 mm. The thread depths is 4.7 mm. The lengths of the screws are 1328 mm and the total processing section length is 1338 mm.

The ZSK-30 extruder has 14 processing barrels, which are numbered consecutively 1 to 14 from the feed barrel to the die for the purposes of this disclosure. In the examples that follow, the first barrel, barrel #1, received the polymer and was cooled by water. The other thirteen barrels are divided into seven heating zones: Zone 1, corresponding to barrels #2, #3 and #4, was set at about 170°C. Zone 2, corresponding to barrels #5 and #6; Zone 3, corresponding to barrels #7 and #8; Zone 4, corresponding to barrels #9 and #10; Zone 5, corresponding to barrels #11 and #12; Zone 6, corresponding to barrels #13 and #14; and Zone 7 corresponding to the die. All of the heating zones were set at about 180°C, except for Examples 15-21 in which Zone 1 was set at about 170°C and the remaining six zones were set at about 180°C. A vacuum port may be used at barrel #11 to remove unreacted monomer.

In the examples that follow, the extruder was run at a screw speed of about 300 rpm. The polymer may be fed into the extruder at the extruder feed throat. The monomer, when added to the molten polymer, was injected into barrel #5 and the initiator was injected into barrel #6. The monomer and the initiator may be injected via pressurized nozzle injectors. The initiator and monomer may be added at the same time or in reverse order. However, the order used in the following Examples is desired. The die used to extrude the modified PEO strands has four openings of 3 mm in diameter, which are separated by 7 mm. The modified PEO strands were extruded onto an air-cooling belt and then pelletized. The extruded PEO melt strands were cooled by air on a fan-cooled conveyor belt 15 feet in length. The pelletizing was performed with a Conair pelletizer.

The polymer, the initiator and the optional monomer(s) may be added simultaneously. For example, the polymer, the initiator and the monomer(s) and may be added together into the hopper of the extruder, barrel #1. It is more desirable to add the polymer to the reactive vessel first and to melt the polymer before adding either the initiator or monomer. Two examples of such methods include (1) melting the base polymer and then injecting a solution comprising initiator and monomer into the molten base polymer; and (2) adding the initiator and then adding the monomer or mixture of monomers to the molten base polymer. It is even more desirable to add and disperse the monomer in the polymer before adding the initiator. Thus, it is desired to add the polymer to the extruder first and then inject and disperse the monomer(s) before adding initiator.

## EXAMPLES

Examples 1-21 use the ZSK-30 extruder as detailed above. The screw speed of the extruder was set at 300 rpm. The barrel temperature was set at 180°C. The PEO resins were fed into the extruder with a K-Tron gravimetric feeder at the throughput reported in Table 1 in pounds per hour. The selected initiator and monomer were fed by Eldex pumps into the extruder at the various rates reported in Table 1. The monomer was fed in barrel #5 and the initiator in barrel #6. The extruded PEO strands were cooled by air on a fan-cooled conveyor belt 15 feet in length and allowed to solidify. The solidified strands were then pelletized in a Conair pelletizer available from Conair of Bay City, Michigan.

Examples A, B, D, F and H are comparative examples of the initial base PEO resin as acquired from the supplier without extrusion or later processing. Examples C, E and G are control examples processed in the ZSK-30 extruder as detailed above but without modification in accordance with the invention. That is, Examples C, E and G were extruded without the addition or use of an initiator for comparison purposes.

The weight percentages of the components used in the Examples were calculated relative to the weight of the base PEO resin, unless otherwise indicated. Five different molecular weights of PEO resins were modified in accordance with the invention. The five PEO resins which were modified included: POLYOX® WSR N-80, WSR 205, WSR 12K, WSR N-301 and WSR N-308 PEO resins having reported initial approximate molecular weights of 200,000, 600,000, 1,000,000, 4,000,000 and 8,000,000 g/mol, respectively, as reported in Union Carbide's product literature. The molecular weights of these polymers as determined by gel permeation chromatography are reported in Table 2 below.

The monomer addition levels of the Examples ranged from as low as 0 weight percent to as high as about 5 weight percent of monomer to the weight of the base resin. The relative amount of initiator used in the Examples varied from 0.11 to 0.51 weight percent of initiator to the weight of the base resin. The trade designation of the base resin, the monomer, and the amounts of base resin, monomer and initiator used in the Examples are listed in Table 1. Comparative Examples A-H represent comparative examples of PEO resins.

Although the present invention is demonstrated by the following Examples, it is to be understood that the PEO, the initiator and the conditions may be varied depending on the type of modified PEO composition and properties desired.

## Table 1

Components and Process Conditions of the Examples

| Example Number | Resin | Resin Rate (lb/hr) | Monomer | Monomer Rate (lb/hr) | Initiator | Initiator Rate (lb/hr) |
|---|---|---|---|---|---|---|
| **A** | unprocessed POLYOX® WSR N-80 | 0 | - | 0 | - | 0 |
| **1** | POLYOX® WSR N-80 | 25 | EHMA | 0.325 | L101 | 0.035 |
| **2** | POLYOX® WSR N-80 | 25 | EHMA | 0.775 | L101 | 0.055 |
| **B** | unprocessed POLYOX® WSR 205 | 0 | - | 0 | - | 0 |
| **C** | processed POLYOX® WSR 205 | 20 | - | 0 | - | 0 |
| **3** | POLYOX® WSR 205 | 25 | EHMA | 1.1 | L101 | 0.027 |
| **4** | POLYOX® WSR 205 | 25 | EHMA | 0.65 | L101 | 0.050 |
| **5** | POLYOX® WSR 205 | 25 | EHMA | 0.375 | L101 | 0.0425 |
| **6** | POLYOX® WSR 205 | 20 | HEMA | 0.60 | L101 | 0.048 |
| **7** | POLYOX® WSR 205 | 20 | HEMA | 0.98 | L101 | 0.056 |
| **8** | POLYOX® WSR 205 | 20 | PEG-MA | 0.62 | L101 | 0.042 |
| **9** | POLYOX® WSR 205 | 20 | PEG-MA | 0.98 | L101 | 0.064 |
| **10** | POLYOX® WSR 205 | 20 | - | 0 | L101 | 0.024 |
| **D** | Unprocessed POLYOX® WSR 12K | 0 | - | 0 | - | 0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **E** | Processed POLYOX® WSR 12K | 20 | - | 0 | - | 0 |
| **11** | POLYOX® WSR 12K | 20 | HEMA | 0.70 | L101 | 0.052 |
| **12** | POLYOX® WSR 12K | 20 | HEMA | 1.00 | L101 | 0.062 |
| **13** | POLYOX® WSR 12K | 20 | PEG-MA | 0.70 | L101 | 0.052 |
| **14** | POLYOX® WSR 12K | 20 | PEG-MA | 1.00 | L101 | 0.064 |
| **15** | POLYOX® WSR 12K | 20 | - | 0 | L101 | 0.024 |
| **F** | Unprocessed POLYOX® WSR N-301 | 0 | - | 0 | - | 0 |
| **G** | Processed POLYOX® WSR N-301 | 20 | - | 0 | - | 0 |
| **16** | POLYOX® WSR N-301 | 20 | HEMA | 0.36 | L101 | 0.102 |
| **17** | POLYOX® WSR N-301 | 20 | HEMA | 0.36 | L101 | 0.056 |
| **18** | POLYOX® WSR N-301 | 20 | HEMA | 0.38 | L101 | 0.034 |
| **19** | POLYOX® WSR N-301 | 20 | HEMA | 0.18 | L101 | 0.036 |
| **H** | Unprocessed POLYOX® WSR N-308 | 0 | - | 0 | - | 0 |
| **20** | POLYOX® WSR N-308 | 20 | HEMA | 0.38 | L101 | 0.034 |
| **21** | POLYOX® WSR N-308 | 20 | HEMA | 0.38 | L101 | 0.056 |
| **22** | POLYOX® WSR N-308 | 20 | HEMA | 0.38 | L101 | 0.084 |

GPC Analysis

The number-average molecular weight ($M_n$), the weight-average molecular weight ($M_w$), and the z-average molecular weight ($M_z$) of the Examples and Comparative Examples were determined by conventional gel permeation chromatography (hereinafter GPC) relative to a PEO calibration curve using PEO standards. From this data, the polydispersity index ($M_w/M_n$) was calculated. The GPC analysis was independently conducted by American Polymer Standards Corporation of Mentor, OH.

Each Example was dissolved in a 0.05 M aqueous solution of $NaNO_3$ and filtered through a 0.5 micron filter before GPC analysis. A 100 μl sample of a solution prepared according to the above procedure containing the polymer of the respective Example was injected into an Ultrahydrogel (1000Å + Linear + 120Å) column at 30°C at a flow rate of 1.0 ml/min. The molecular weights of the Examples 1-5 were determined by the same procedure but injected into an Ultrahydrogel (2-hydroxyethyl methacrylate AM GEL Linear + 120Å) column under the same conditions. The molecular weights of Comparative Example A were determined in a 0.1 M $NaNO_3$, 0.1 percent ethylene glycol solution in a Ultrahydrogel (2 2-HEMA 2T Linears) column. The molecular weights were measured using a Knauer DRI detector at 8X. The results of the GPC analysis of each of the respective Examples are reported in Table 2 below.

## Table 2

Molecular Weights and Polydispersity Indices
as determined by GPC Relative to the PEO Standards

| Example | $M_n$ | $M_w$ | $M_z$ | $M_w / M_n$ |
|---|---|---|---|---|
| A | 12,650 | 148,100 | 840,500 | 11.71 |
| 1 | 21,000 | 77,350 | - | 3.68 |
| 2 | 20,200 | 82,650 | - | 4.09 |
| B | 77,400 | 1,000,000 | 6,560,000 | 12.92 |
| C | 46,500 | 582,000 | 4,470,000 | 12.52 |
| 3 | 21,150 | 92,400 | - | 4.37 |
| 4 | 21,800 | 86,750 | - | 3.98 |
| 5 | 26,250 | 97,250 | - | 3.70 |
| 6 | 44,200 | 227,900 | 1,100,000 | 5.16 |
| 7 | 48,800 | 224,700 | 1,100,000 | 4.60 |
| 8 | 44,100 | 179,400 | 780,000 | 4.07 |
| 9 | 47,200 | 210,500 | 940,000 | 4.46 |
| 10 | 29,600 | 99,800 | 185,900 | 3.37 |
| D | 56,000 | 1,120,000 | 7,890,000 | 20.00 |
| E | 47,000 | 671,800 | 6,060,000 | 14.29 |
| 11 | 55,800 | 248,100 | 1,140,000 | 4.45 |
| 12 | 57,800 | 279,800 | 1,340,000 | 4.84 |
| 13 | 45,900 | 211,600 | 1,650,000 | 4.61 |
| 14 | 52,400 | 213,200 | 1,500,000 | 4.07 |
| 15 | 30,200 | 96,900 | 182,900 | 3.21 |
| F | 693,000 | 1,477,000 | 2,267,000 | 2.13 |
| G | 190,100 | 1,010,000 | 2,449,000 | 5.31 |
| 16 | 31,400 | 181,900 | 460,900 | 5.79 |
| 17 | 36,200 | 166,600 | 410,300 | 4.60 |
| 18 | 31,100 | 196,600 | 480,300 | 6.32 |
| 19 | 37,000 | 139,200 | 328,400 | 3.76 |
| H | 445,600 | 1,530,000 | 2,513,000 | 3.43 |
| 20 | 37,900 | 178,600 | 429,300 | 4.71 |
| 21 | 36,900 | 162,200 | 398,400 | 4.40 |
| 22 | 26,900 | 99,900 | 265,200 | 3.71 |

Examples 1-22 demonstrate significant reductions in the weight-average molecular weight ($M_w$) of the PEO resin after extrusion with an initiator compared to the base PEO resins, Comparative Examples A, B, D, F and H, and the base PEO resins extruded without the addition of initiator. For example, the $M_w$ of Comparative Example A was reduced by more than 44 percent in Examples 1 and 2, after extrusion with an initiator. The $M_W$ of Comparative Example B was reduced by 77 to 91 percent in Examples 3-10, after extrusion with initiator. Comparative Example C demonstrated a reduction in $M_W$ after extrusion without initiator also. However, the reduction in $M_W$ was only 42 percent compared to greater than 77 percent for molecular weight reduction by extrusion with initiator and does not demonstrate a significant reduction in polydispersity index as observed in extrusion with initiator.

Compared to Example D, the weight-average molecular weight of the base PEO resin was reduced from 75 to 91 percent after reactive-extrusion with initiator. Whereas, the weight-average molecular weight was reduce by only 40 percent after extrusion without initiator, Example E. Similar results were observed for the reactive-extrusion of the POLYOX® WSR N-301 PEO resin of Examples 15-17 and F and G. After reactive-extrusion with initiator, the weight-average molecular weight was reduced by 87 to 91 percent compared to only a 32 percent reduction in weight-average molecular weight after extrusion without initiator.

Suprisingly, the polydispersity indices of polymers modified from PEO resins with starting molecular weights of less than 4,000,000 g/mol were reduced by reactive-extrusion with an initiator and optional monomer. Reduced polydispersity indices were observed in Examples 1-9 and 11-14, corresponding to PEO base resins having initial molecular weights ranging from the nominal 200,000 g/mol to 1,000,000 g/mol PEO resins. These low weight PEO base resins were previously modified by the supplier using prior art methods and initially had high polydispersity indices ranging form 11.71 to 20.00. The method of the present invention produced even lower molecular weight polymer compositions with reduced polydispersity indices, ranging from 3.21 to 5.16 for the same PEO base resins. Thus, the present invention provides a method of reducing the polydispersity indices of PEO resins from prior art-modified PEO resins.

Remarkable narrowing in molecular weight distributions was observed in the reduction of the polydispersity indices. For instance, the polydispersity index of POLYOX® WSR 205 PEO resin decreased from 12.92 down to 4.37 for Example 3 and to as low as 3.37 for Example 10. The polydispersity index of POLYOX® WSR N-80 PEO decreased from 11.71 to 3.68 for Example 1 and 4.09 for Example 2. The polydispersity index of POLYOX® WSR 12K PEO decreased from 20.00 to 3.21-4.84 for Examples 11-15.

Examples 10 and 15 show molecular weight reductions without the addition of optional monomer. Note that both the average molecular weights, $M_n$, $M_w$, and $M_z$, and the polydispersity of the polymers produced in these two examples without monomer were significantly reduced as compared to Example 1-9 and 11-14.

Examples 16-19 and 20-22 show molecular weight reductions for higher molecular weight starting resins that had not been previously reduced by the supplier using prior art methods. These PEO resins had nominal starting average molecular weights of 4,000,000 and 8,000,00 g/mol, respectively. Note that the resulting reduced PEO compositions have significantly reduced molecular weights as well as reduced polydispersity indices, surprisingly lower than similar resins produced by irradiation degradation, Comparative Examples A-E.

The modification of the lower molecular weight PEO resins of Examples 1 and 2 brought about an increase in the number-average molecular weight and a reduction in the weight-average molecular weight, thus, reducing the polydispersity index. The change in the molecular weights and molecular weight distributions was unexpected.

The present invention demonstrates a process in which the molecular weights are significantly reduced and the polydispersity index is reduced or at least retained at a low level for all PEO resins. No other process has demonstrated how to keep both molecular weights and polydispersity indices at a low level. Along with the unexpected changes in molecular weights and the polydispersity indices, vast improvement in the melt processabilities of the PEO resins was also observed as demonstrated below.

Solution Viscosity Analysis

The solution viscosity of several of the examples were assessed on a Brookfield RVTD viscometer. A five weight percent aqueous solution of the example to be tested was prepared by placing 5 grams of the example in 475 ml of distilled water and stirring at room temperature until the resin pellets were fully dissolved. From this data, the polydispersity index ($M_w/M_n$) of the example was calculated. Spindle number and speed were selected based on applicable viscosity range. The solution viscosity results of the examples analyzed in this manner are reported in Table 3 below.

## Table 3

Solution Viscosity

| Example | Spindle Number | Speed (rpm) | Viscosity Range (cp) | Average Viscosity (cp) | Average Reduction in Viscosity |
|---|---|---|---|---|---|
| A | 1 | 50 | 66.2-66.4 | 66.3 | - |
| 1 | 1 | 50 | 23.8-54 | 23.9 | 64.0 % |
| 2 | 1 | 50 | 24.6-25 | 24.8 | 62.6 % |
| B | 2 | 50 | 5104-5232 | 5,168 | - |
| 3 | 1 | 50 | 35.2-35.6 | 35.4 | 99.3 % |
| 4 | 1 | 50 | 45.4-45.8 | 45.6 | 99.1 % |
| 5 | 1 | 50 | 43.8-44 | 43.9 | 99.2 % |
| 6 | 1 | 50 | 115-115.4 | 115.2 | 97.8 % |
| 7 | 1 | 50 | 89.4-89.6 | 89.5 | 98.3 % |
| 9 | 1 | 50 | 81-81.4 | 81.2 | 98.4 % |
| D | 2 | 1 | 23560-23840 | 23,700 | - |
| 11 | 1 | 50 | 109-109.2 | 109.1 | 99.5 % |
| 12 | 1 | 50 | 136.6-136.8 | 136.7 | 99.4 % |
| 14 | 1 | 50 | 79.8-80 | 79.9 | 99.7 % |

The measured viscosities of the modified PEO solutions were much lower than the corresponding unmodified PEO solutions. The unmodified POLYOX® WSR N-80 of Example A had a solution viscosity of 66.3 centipoise (cp). Whereas, Examples 1 and 2 and had an average solution viscosity of 23.9 cp and 24.8 cp, respectively. Modification with 1.3 weight percent monomer and 0.22 weight initiator resulted in a 64 percent reduction in viscosity. After reactive extrusion, with 3.1 weight percent EHMA monomer and 0.28 weight percent L101 initiator the resulting modified PEO, Example 2, has a solution viscosity of 24.8 cp, a 62.6 percent reduction in viscosity compared to the unmodified PEO resin.

The viscosities of the POLYOX® WSR-205 and POLYOX® WSR N-12K resins were even more dramatically reduced by modification in accordance with the invention. The solution viscosities of the unmodified POLYOX® WSR-205 and unmodified POLYOX® WSR N-12K resins were 5,168 cp and 23,700 cp, respectively. After modification, the solution viscosity was reduced by over 97 percent. Such reduced viscosities permit the modified polymers to be more easily and economically processed. The lowest viscosity achieved by modifying a POLYOX® WSR-205 resin was 35.4 cp for Example 3. This low viscosity is 145 times lower that the viscosity of the corresponding, unmodified control example, Example B. On average, the solution viscosities of the grafted POLYOX® WSR N-12K PEO compositions, Examples 11, 12 and 14, were 215 times lower than the POLYOX® WSR N-12K control, Example D.

The fundamental changes in reduced weight PEO brought about by the method of the invention have profound and unexpected effects on the physical properties and melt processability of PEO. The narrower molecular weight distributions of the modified PEO compositions result in improved melt and solid state properties. Although the molecular weight reduction and polydispersity reduction methods were developed primarily for PEO resins to be used in melt-based applications, PEO resins may be improved by the method of the invention for solution-based applications as well.

Not wishing to be bound by the following theory, it is believed that during the processing of PEO resin, the initiator promotes two competing reactions: (1) degradation of the PEO and (2) crosslinking of the PEO. Appreciable crosslinking results in the inclusion of a crosslinked and insoluble polymer fraction. However, the molecular weights of the soluble fraction are reduced. The optional addition of monomer to the reactive-extrusion process adds a third competing reaction, (3) grafting of monomer onto the PEO, which significantly decreases the degree of crosslinking, producing a predominantly soluble and thermally processable composition.

Extrusion Processability Analysis

The extrusion processability of several of the Examples was assessed using the same extrusion apparatus and configuration as described above to produce the Examples. The process data for the tested Examples was recorded during extrusion and reactive-extrusion. The data is presented in Table 4 below. The PEO resins produced in accordance with the present invention demonstrate reduced percent torque, reduced energy consumption, reduced melt temperature, and reduced melt pressure thereby allowing higher production and processing rates compared to corresponding unmodified PEO base resins. The observed process data supports the observation that the reduced molecular weight and the reduced polydispersity indices of modified PEOs result in improved processability and safety during extrusion.

## Table 4

Process Data for Extrusion

| Example | Torque (%) | Melt Temperature (°C) | Melt Pressure (psi) |
|---|---|---|---|
| B | 34 | 204 | 1830 |
| 6 | 30 | 196 | 1102 |
| 7 | 30 | 189 | 1030 |
| 8 | 27 | 192 | 715 |
| 9 | 29 | 192 | 765 |
| 10 | 26 | 198 | 313 |
| D | 42 | 209 | 1600 |
| 11 | 29 | 190 | 1032 |
| 12 | 31 | 187 | 1125 |
| 13 | 28 | 191 | 745 |
| 14 | 30 | 186 | 773 |
| F | 58 | 224 | 1272 |
| 16 | 53 | 214 | 544 |
| 17 | 48 | 210 | 454 |
| 18 | 52 | 212 | 627 |

Examples 6-10 compared to the unmodified, control Example B demonstrated: reduced torque, by 4 to 8 percent; reduced melt temperature, by 6°C to 15°C; and reduced melt pressure, by 728 psi to 1517 psi, a 40 to 83 percent reduction. Examples 11-14 compared to the unmodified, control Example D demonstrated: reduced torque, by 11 to 14 percent; reduced melt temperature by 18°C to 23°C; and reduced melt, by 475 psi to 855 psi, a 30 to 50 percent reduction. Examples 16-18 compared to the unmodified, control Example F demonstrated: reduced torque, by 5 to 10 percent; reduced melt temperature by 10°C to 24°C; and reduced melt pressure, by 645 psi to 818 psi, a 50 to 64 percent reduction. Each of the tested weight reduced PEO Examples showed a measurable reduction in torque, melt temperature and melt pressure compared to the unmodified PEO resins from which the respective Examples were produced.

The present invention has been illustrated in great detail by the above specific Examples. It is to be understood that these Examples are illustrative embodiments and that this invention is not to be limited by any of the Examples or details in the Description. Those skilled in the art will recognize that the present invention is capable of many modifications and variations without departing from the scope of the invention. Accordingly, the Detailed Description and Examples are meant to be illustrative and are not meant to limit in any manner the scope of the invention.

**We Claim:**

1. A method for reducing the molecular weight of a polymer of ethylene oxide comprising:

adding a polymer of ethylene oxide and an initiator into a reaction vessel; and

mixing the polymer of ethylene oxide and the initiator under conditions sufficient to reduce the molecular weight of the polymer of ethylene oxide.

2. The method of Claim 1, wherein the initiator is a free radical initiator that generates free radicals at a temperature of less than about 220°C.

3. The method of Claim 1, wherein the conditions sufficient to reduce the molecular weight of the polymer of ethylene oxide comprise heating the polymer of ethylene oxide and the initiator to a temperature of greater than about 80°C.

4. The method of Claim 1, wherein the conditions sufficient to reduce the molecular weight of the polymer of ethylene oxide comprise heating the polymer of ethylene oxide and the initiator to a temperature within the range of from the melting point of the polymer of ethylene oxide to the decomposition temperature of the polymer of ethylene oxide.

5. The method of Claim 2, wherein the conditions sufficient to reduce the molecular weight of the polymer of ethylene oxide comprise heating the polymer of ethylene oxide and the free radical initiator to a temperature within the range from about 120°C to about 220°C.

6. The method of Claim 1, wherein at least one vinyl monomer is further added to the polymer of ethylene oxide and the initiator, wherein vinyl monomer includes both polar and nonpolar vinyl monomers.

7. The method of Claim 1, wherein the initiator is added within the range of from about 0.05 to about 2 weight monomer percent relative to weight of the polymer of ethylene oxide.

8. The method of Claim 7, wherein the initiator is added within the range of from about 0.1 to about 1 weight percent monomer relative to weight of the polymer of ethylene oxide.

9. The method of Claim 8, wherein the initiator is added within the range of about 0.1 to about 0.5 weight percent relative to the weight of the polymer of ethylene oxide.

10. A polymer of ethylene oxide with a reduced molecular weight produced by the method of Claim 1.

11. The polymer of ethylene oxide Claim 10, wherein the polymer of ethylene oxide has a weight-average molecular weight of less than 1,000,000 grams per mol.

12. The polymer of ethylene oxide of Claim 10, wherein the polymer of ethylene oxide has a polydispersity index of less than 10.

13. The polymer of ethylene oxide of Claim 10, wherein the polymer of ethylene oxide has a polydispersity index of less than 7.

14. A method for reducing the molecular weight of a polymer composition consisting essentially of:

adding a polymer composition and an initiator into a reaction vessel; and

mixing the polymer composition and the initiator under conditions sufficient to reduce the molecular weight of the polymer composition, wherein the conditions sufficient to reduce the molecular weight of the polymer composition comprise heating the polymer composition and the initiator to a temperature within the range of from the melting point of the polymer composition to the decomposition temperature of the polymer composition.

15. The method of Claim 14, wherein the polymer composition consists essentially of a polymer or copolymer of ethylene oxide.

16. The method of Claim 14, wherein the polymer composition consists essentially of poly(ethylene oxide).

17. A method of reducing the polydispersity index of a polymer of ethylene oxide comprising:

adding a polymer of ethylene oxide and an initiator into a reaction vessel; and

mixing the polymer of ethylene oxide and the initiator under conditions sufficient to reduce the polydispersity index of the polymer of ethylene oxide.

18. The method of Claim 17, wherein the polymer of ethylene oxide is polymer of ethylene oxide having a molecular weight that was reduced by irradiation prior to adding to the initiator and mixing.

19. A polymer of ethylene oxide with a polydispersity index reduced by the method of Claim 17.

20. A method of pelletizing a polymer of ethylene oxide comprising:

feeding a polymer of ethylene oxide and an initiator into an extruder;

creating a mixture of the polymer of ethylene oxide and the initiator under melt conditions;

extruding the mixture;

cooling the mixture; and

pelletizing the mixture.

21. The method of Claim 20, further comprising feeding a monomer into the extruder.

22. The method of Claim 21, wherein the monomer is fed into the extruder after the polymer is fed into the extruder and before the initiator is fed into the extruder.

23. The method of Claim 20, wherein the initiator is added within the range of from about 0.05 to about 2 weight monomer percent relative to weight of the polymer of ethylene oxide.

24. Pellets of a polymer of ethylene oxide produced by the method of Claim 20.

# INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 98/27836

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 C08G65/30 C08G65/32 C08F283/06 C08L71/02

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)
IPC 6 C08G C08F C08L

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)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| X | US 4 200 704 A (ANDERSON DONALD F ET AL) 29 April 1980<br>cited in the application<br>see claim 5; example 5 | 1-3,9-11 |
| X | EP 0 515 949 A (BAYER AG) 2 December 1992<br>see example 1 | 10-13 |
| X | DE 18 06 165 A (HERCULES INC.) 29 May 1969<br>see examples 3,4 | 1-5, 9-11,14, 15 |

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

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|---|---|
| Date of the actual completion of the international search<br>29 March 1999 | Date of mailing of the international search report<br>12/04/1999 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>O'Sullivan, T |

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# INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication,where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | EP 0 461 785 A (ARCO CHEM TECH)<br>18 December 1991<br><br>see table 1<br>see example 7<br>see claims 1-6<br>----- | 1-3,<br>10-13,<br>17,19 |

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Inter   ›nal Application No
PCT/US 98/27836

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