oxide tends to polymerize to form extremely high molecular materials when DMC catalysts are used.

Although much of the patent literature concerning DMC catalysis mentions 1,2-butylene oxide as an alkylene oxide which can be polymerized using those catalyst, virtually no examples of such polymerizations are described in the literature. This may be due to the fact that 1,2-butylene oxide does not form significant quantities of monofunctional species when anionically polymerized under conventional basic conditions, so much of the impetus that drove the adoption of DMC catalysis into making poly(propylene oxide) does not exist in the case of 1,2-butylene oxide polymerization. JP H6-248069 (1994) contains examples of propylene oxide copolymerized with small amounts of 1,2- or 2,3-butylene oxide. The resulting polyethers contain about 5% or less of polymerized butylene oxide.

Therefore, the polymerization behavior of 1,2-butylene oxide in the presence of a polyfunctional initiator compound and a DMC catalyst is heretofore unknown.

This ~~invention~~ disclosure is ~~in one aspect~~ a process for producing poly(1,2-butylene oxide) polymers, comprising polymerizing 1,2-butylene oxide or a mixture of at least 50% by weight 1,2-butylene oxide and up to 50% by weight of a copolymerizable alkylene oxide in the presence of a double metal cyanide catalyst and in the presence of a hydroxylic initiator compound to form a polymer or copolymer of 1,2-butylene oxide having at least one block of homopolymerized or randomly copolymerized 1,2-butylene oxide having a number average weight of at least 500 atomic mass units.

In one aspect, the present disclosure provides a process for producing poly(1,2-butylene oxide) polymers, comprising polymerizing 1,2-butylene oxide or a mixture of at least 50% by weight 1,2-butylene oxide and up to 50% by weight of a copolymerizable alkylene oxide at a polymerization temperature of 90 to 160°C in the presence of enough of a double metal cyanide catalyst to provide a cobalt concentration of 1 to 6 parts per million in the product and in the presence of a hydroxylic initiator compound to form a polymer or copolymer of 1,2-butylene oxide having at least one block of homopolymerized or randomly copolymerized 1,2-butylene oxide having a number average weight of at least 500 atomic mass units and which contains no more than 25 microequivalents per gram of monofunctional, unsaturated species.

Mass of a block in atomic mass units is equivalent to the same number of grams of such block per mole of the poly(1,2-butylene oxide) polymer.

Applicants have found that when 1,2-butylene oxide is homopolymerized using a DMC catalyst, very little butadiene is produced. This is a distinct advantage over the conventional anionic polymerization of 1,2-butylene oxide. However, the product very surprisingly contains a significant amount of monofunctional species. This result is exactly contrary to what is seen when propylene oxide is polymerized with those catalysts, and is quite unexpected in view of the experience with propylene oxide polymerization. The formation of monofunctional species is of course a very substantial disadvantage for the reasons discussed above.

Applicants have further discovered that the amount of monofunctional species can be controlled and somewhat minimized by the selection of certain parameters during the polymerization, in particular the polymerization temperature and the level of DMC catalyst. Therefore, in certain embodiments, this ~~invention~~ disclosure is a process for producing poly(1,2-butylene oxide) polymers, comprising polymerizing 1,2-butylene oxide or a mixture of at least 50% by weight 1,2-butylene oxide and up to 50% by weight of a copolymerizable alkylene oxide at a polymerization temperature of 90 to 160°C in the presence of a hydroxylic initiator compound and enough of a zinc hexacyanocobaltate catalyst complex to provide a cobalt concentration of 1 to 6 parts per million in the product, to form a polymer or copolymer of 1,2-butylene oxide having at least one block of homopolymerized or randomly copolymerized 1,2-butylene oxide, said at least one block having a number average weight of 800 to 2500 atomic mass units, wherein the polymer or copolymer contains no more than 25 microequivalents per gram of monofunctional, unsaturated species.

In other specific embodiments, this disclosure ~~invention~~ is a process for producing poly(1,2-butylene oxide) polymers, comprising polymerizing 1,2-butylene oxide or a mixture of at least 50% by weight 1,2-butylene oxide and up to 50% by weight of a copolymerizable alkylene oxide at a polymerization temperature of 90 to 160°C in the presence of a hydroxylic initiator compound and enough of a zinc hexacyanocobaltate catalyst complex to provide a cobalt concentration of 1 to 6 parts per million in the product, to form a polymer or copolymer of 1,2-butylene oxide having at least one block of homopolymerized or randomly copolymerized 1,2-butylene oxide, said at least one block having a number average weight of 2501 to 4500 atomic mass units, wherein the polymer or copolymer contains no more than 75 microequivalents per gram of monofunctional, unsaturated species.

In another aspect, the present disclosure provides a poly(1,2-butylene oxide) polymer made in accordance with the aspect above.

In another ~~-~~embodiment~~aspect~~, this disclosure~~invention~~ is a polymer or copolymer of 1,2-butylene oxide having at least one block of homopolymerized 1,2-butylene oxide having a number average weight of 800 to 4500 atomic mass units and/or at least one block of randomly copolymerized 1,2-butylene oxide having a number average weight of 800 to 4500 atomic mass units which randomly copolymerized block contains at least 50 weight percent polymerized 1,2-butylene oxide, wherein the polymer or copolymer contains 1 to 6 parts per million of cobalt residue from a zinc hexacyanocobaltate catalyst complex and no more than 75 microequivalents per gram of monofunctional, unsaturated species. In some embodiments, such a

polymer or copolymer has at least one block of homopolymerized 1,2-butylene oxide having a number average weight of 2501 to 4500 atomic mass units and/or at least one block of randomly copolymerized 1,2-butylene oxide having a number average weight of 2501 to 4500 atomic mass units which randomly copolymerized block contains at least 50 weight percent polymerized 1,2-butylene oxide. In other embodiments, such a polymer or copolymer has at least one block of homopolymerized 1,2-butylene oxide having a number average weight of 800 to 2500 atomic mass units and/or at least one block of randomly copolymerized 1,2-butylene oxide having a number average weight of 800 to 2500 atomic mass units, which randomly copolymerized block contains at least 50 weight percent polymerized 1,2-butylene oxide, and the polymer or copolymer contains no more than 25 microequivalents per gram of monofunctional, unsaturated species.

In some embodiments of the disclosure~~invention~~, 1,2-butylene oxide is homopolymerized. By "homopolymerized", it is meant that the 1,2-butylene oxide is polymerized by itself to form a polymer having at least one poly(1,2-butylene oxide) block having a number average weight of at least 500 atomic mass units.

In other embodiments, 1,2-butylene oxide is randomly or pseudo-randomly copolymerized with up to 50% by weight, based on total weight of monomers, with one or more copolymerizable monomers to form polymer having at least one random or pseudo-random copolymer block having a weight of at least 500 atomic mass units. Random or pseudo-random polymerization is performed in the simultaneous presence of 1,2-butylene oxide and the other monomer(s). If randomly or pseudo-randomly copolymerized, the mixture of monomer preferably contains at least 75%, more preferably at least 90% and still more preferably at least 95% by weight 1,2-butylene oxide.

The block or blocks of homopolymerized or copolymerized 1,2-butylene oxide may have a number average weight of up to 10,000 atomic mass units. In some embodiments, they have a number average weight of 800 to 4000, 800 to 2500 or 2501 to 4000 atomic mass units. When the product is a polyol intended for use in polyurethane applications, the blocks preferably have number average weights of at least 500, more preferably at least 750, and still more preferably at least 800, up to 3000, more preferably up to 2500, still more preferably up to 2000 and even more preferably up to 1500 atomic mass units.

In addition to the blocks of homopolymerized or copolymerized 1,2-butylene oxide blocks, the polymer may contain one or more other blocks.