INHIBITOR COMBINATION FOR LITHIUM SALT-CATALYZED TRANSESTERIFICATION PROCESS AND METHOD FOR REMOVING LITHIUM SALT

BACKGROUND OF THE INVENTION

[0001] Lithium hydroxide is a known transesterification catalyst for making methacrylate ester monomers via reaction of methyl methacrylate (MMA) with specialty alcohols (for example, see US 6,048,916, GB 1,094,998, US 5,072,027, US 4,916,255, US 4,672,105, JP 2007055910A). Inhibitors are typically employed in these reactions to keep the monomers from polymerizing during processing. Inhibitors often include, among others, the methyl ether of hydroquinone (MeHQ) and/or phenothiazine (PTZ).

[0002] There is continued interest in developing inhibitor combinations which allow the transesterification process to proceed at higher rates while maintaining excellent long term monomer product stability.

[0003] When these transesterification reactions are complete, the catalyst is often removed via filtration procedures that include the addition of either some solid filtration agent (such as diatomaceous earth; in addition to above references, also see JP03109350A) or a hydrocarbon solvent (see JP3106847A) to aid in precipitation and/or removal of the precipitated lithium salts. These filtration agents and solvents, however, create more waste and increase disposal costs.

[0004] There also remains a need for a process to remove the lithium catalyst (i.e., lithium salt) without the addition of filtration agents or solvents.

SUMMARY ~~OF THE INVENTION~~

[0005] The ~~invention~~ disclosure provides a transesterification process to form a composition comprising an asymmetrical polyene, the asymmetrical polyene comprising an "α,β unsaturated – carbonyl end" and a "C-C double bond end," the process comprising reacting an alkene- or polyene-containing alcohol with an alkyl ester of an alpha, beta unsaturated carboxylic acid in the presence of at least the following components A) through C), to form a solution comprising the asymmetrical polyene:

A) a lithium salt;

B) a component selected from the group consisting of hydroquinone, an alkyl-substituted phenol, a substituted alkyl-substituted phenol, an alkyl-

substituted hydroquinone, a substituted alkyl-substituted hydroquinone, and combinations thereof; and

C) an N-oxyl-containing compound;

wherein the "α,β unsaturated – carbonyl end" of the asymmetrical polyene is selected from the group consisting of structures a) through c), as described herein, and wherein the "C-C double bond end" of the asymmetrical polyene is selected from the group consisting of structures 1) through 17), as described herein.

[0005a] In a first aspect, there is provided a process to form a composition comprising an asymmetrical polyene, the asymmetrical polyene comprising an "α,β unsaturated – carbonyl end" and a "C-C double bond end," the process comprising:

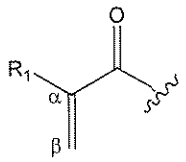
reacting an alkene- or polyene-containing alcohol with an alkyl ester of an α,β unsaturated carboxylic acid in the presence of at least the following components A) through C) to form a solution comprising the asymmetrical polyene:

A) a lithium salt;

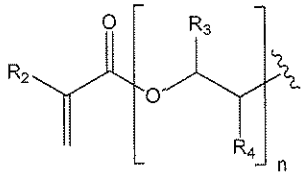
B) a component selected from the group consisting of hydroquinone, an alkyl-substituted phenol, a substituted alkyl-substituted phenol, an alkyl-substituted hydroquinone, a substituted alkyl-substituted hydroquinone, and combinations thereof; and

C) an N-oxyl-containing compound;

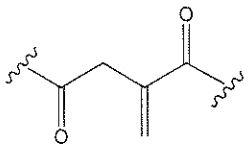
wherein the "α,β unsaturated – carbonyl end" of the asymmetrical polyene is selected from the group consisting of the following:

a) 

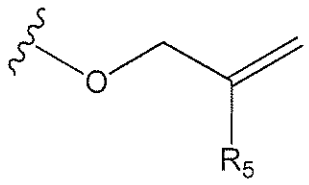
, wherein R_1 is selected from H or a C_1-C_6 alkyl (preferably a C_1-C_3 alkyl and more preferably CH_3);

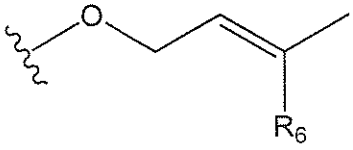
b) 

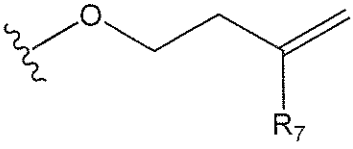
, wherein R_2 is selected from H or a C_1-C_6 alkyl (preferably a C_1-C_3 alkyl and more preferably CH_3); R_3 is selected from H, CH_3, or CH_2CH_3; R_4 is selected from H, CH_3, or CH_2CH_3; and n is from 1 to 50, or from 1 to 20, or further from 1 to 10; and

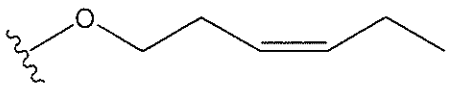
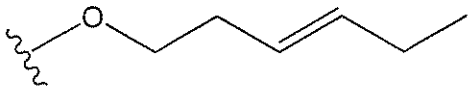
c)  ; and

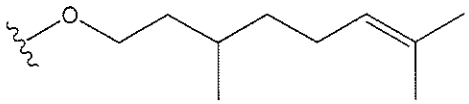
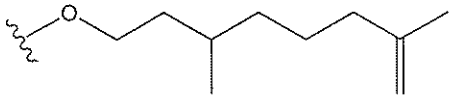
wherein the "C-C double bond end" of the asymmetrical polyene is selected from the group consisting of the following:

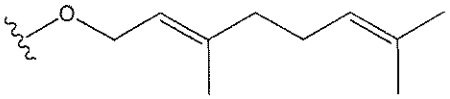
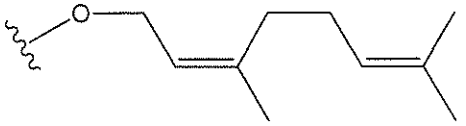
1)  , wherein R5 is selected from H or C1-C6 alkyl;

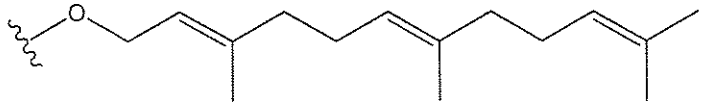
2)  , wherein R6 is selected from H or C1-C6 alkyl;

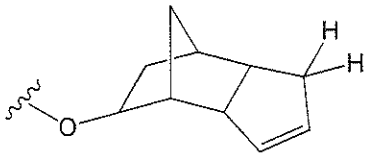
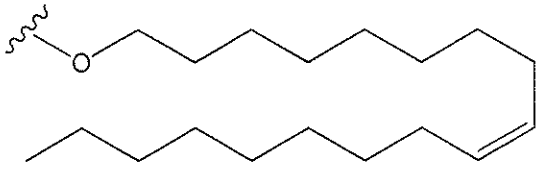
3)  , wherein R7 is selected from H or C1-C6 alkyl;

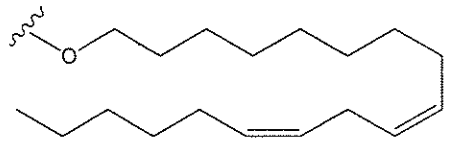
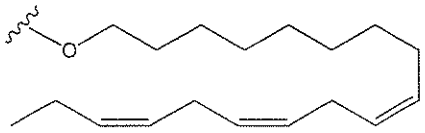
4)  ; 5)  ;

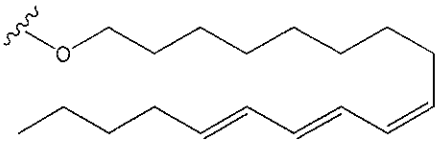
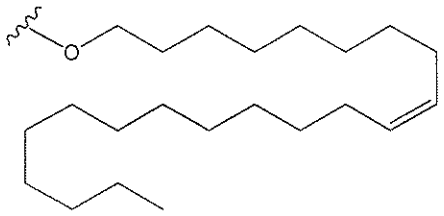
6)  ; 7)  ;

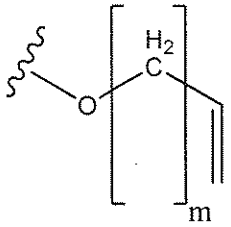
8)  ; 9)  ;

10)  ;

11)  ; 12)  ;

13)  ; 14)  ;

15)  ; 16)  ; and

17)  , wherein m = 1 to 20.

[0005b] In a second aspect, there is provided a composition comprising an asymmetrical polyene formed by the process as defined herein, and wherein the composition comprises less than 100 ppm of an inhibitor selected from the group consisting of 4-HT and derivatives thereof, and less than 2000 ppm of MeHQ, each based on the weight of the composition.

[0005c] In a third aspect, there is provided an asymmetrical polyene formed from the process as defined herein.

[0005d] In a forth aspect, there is provided an ethylene-based polymer formed from the composition comprising ethylene and the asymmetrical polyene as defined herein.

[0005e] In a fifth aspect, there is provided an article comprising at least one component formed from the polymer as defined herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0006] In one embodiment the invention is a process to form a composition comprising an asymmetrical polyene, the asymmetrical polyene comprising an "α,β unsaturated – carbonyl end" and a "C-C double bond end," the process comprising reacting an alkene- or polyene-containing alcohol with an alkyl ester of an α,β unsaturated carboxylic acid in the presence of at least the following components A) through C), to form a solution comprising the asymmetrical polyene:

A) a lithium salt;

B) a component selected from the group consisting of hydroquinone, an alkyl-substituted phenol, a substituted alkyl-substituted phenol, an alkyl-substituted hydroquinone, a substituted alkyl-substituted hydroquinone, and combinations thereof; and

C) an N-oxyl-containing compound;

wherein the "α,β unsaturated – carbonyl end" of the asymmetrical polyene is selected from the group consisting of structures a) through c), as described herein, and wherein the "C-C double bond end" of the asymmetrical polyene is selected from the group consisting of structures 1) through 17), as described herein.

[0007] An inventive process may comprise a combination of two or more embodiments described herein.

Alkene- or Polyene-Containing Alcohol

[0008] In one embodiment, the transesterification process of the present invention produces an asymmetrical polyene and involves a first step of reacting an alkene- or polyene-containing alcohol with an alkyl ester of an α,β unsaturated carboxylic acid. The term "alkene- or polyene-