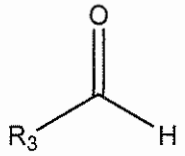
SUMMARY OF THE ~~INVENTION~~DISCLOSURE

An aspect of the present ~~invention~~disclosure is directed to a method for functionalizing polyolefins with hydroxyl group(s). More particularly, the method is directed to where a vinylidene terminated polyolefin is functionalized via the carbonyl-ene reaction with a reactive aldehyde in the presence of a Lewis acid. Thus, one aspect is directed to a method for preparing a hydroxyl functionalized polymer from a Lewis acid promoted carbonyl-ene reaction comprising:

a. selecting a vinylidene terminated polyolefin having a number average molecular weight from about 950 to about 5000 and having a terminal vinylidene content greater than 50 mole percent;
b. selecting a carbonyl enophile;
c. selecting a Lewis acid; and
d. contacting the components in step a), b) and c) under reactive conditions to form the hydroxyl functionalized polymer.

Suitable vinylidene terminated polyolefins are polymers or copolymers of mono-olefins, particularly 1-mono-olefins, such as ethylene, propylene, butylene, and the like. Preferably, the mono-olefin employed will have from about 2 to about 24 carbon atoms, and more preferably, from about 3 to about 12 carbon atoms. More preferred mono-olefins include propylene, butylene, particularly isobutylene. In one aspect, the vinylidene terminated polyolefin is selected from the groups consisting of polypropylene, polyisobutylene, poly-1-butene, copolymer of ethylene and isobutylene, copolymer of propylene and isobutylene, poly-1-pentene, poly-4-methyl-1-pentene, poly-1-hexene, poly-3-methylbutene-1, and polyisoprene. In a preferred aspect, the vinylidene terminated polyolefin has a number average molecular weight from about 700 to about 3,000. Particularly preferred vinylidene terminated polyolefins are derived from isobutylene.

A preferred carbonyl enophile is electron deficient containing a suitable electron withdrawing substituent that withdraws electron density either through inductive or resonance effects from the carbonyl group. In this regard, a more preferred carbonyl enophile is a reactive aldehyde of the aldehydes having the structure,



wherein R_3 can be hydrogen, haloalkyl, alkoxycarbonyl and aryl substituted with at least one electron withdrawing group selected from nitro, cyano, and alkoxycarbonyl.

In a first aspect, there is provided a method for preparing a hydroxyl functionalized polymer from a Lewis acid promoted carbonyl-ene reaction comprising:

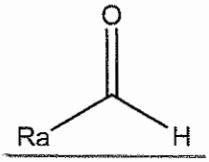
a. selecting a vinylidene terminated polyolefin having a number average molecular weight from about 950 to about 5000 and having a terminal vinylidene content greater than 50 mole percent;

b. selecting a carbonyl enophile;

c. selecting a Lewis acid; and

d. contacting the components in step a), b) and c) under reactive conditions to form the hydroxyl functionalized polymer,

wherein the carbonyl enophile is a reactive aldehyde of the formula:



wherein R_a is selected from the group consisting of hydrogen, haloalkyl, alkoxycarbonyl and aryl substituted with at least one electron withdrawing group selected from nitro, cyano, and alkoxycarbonyl.

In one aspect a reactive aldehyde is formaldehyde or paraformaldehyde. In another aspect the reactive aldehyde is selected from the group consisting of methyl glyoxylate, ethyl glyoxylate, isopropyl glyoxylate, n-butyl glyoxylate, and t-butyl glyoxylate. In a further aspect the reactive aldehyde is a benzaldehyde or substituted benzaldehyde being substituted with at least one electron withdrawing group selected from nitro, cyano and alkoxycarbonyl wherein the alkyl group is from 1 to 6 carbon atoms.

The carbony-ene reaction is promoted by a Lewis acid and the Lewis acid may be catalytic Lewis acids which are not consumed in the carbonyl-ene reaction or they may stoichiometric type Lewis acids which are consumed during the carbony-ene reaction (which is shown in Scheme 4, herein). Catalytic Lewis acids may lead to bis addition products and mixtures therein. While the stoichiometric type Lewis acids give primarily mono-addition products. Accordingly, in one aspect the Lewis acid is of the formula $R'_yAlX_{(3-y)}$ where R′ is a C_{1-6} alkyl; X is halogen: and y is an integer from 1 to 2. Particularly preferred alkyl groups are methyl and ethyl groups. A particularly preferred halogen is chlorine. Suitable Lewis acids are selected from at least one of Me_2AlCl and $EtAlCl_2$. In another aspect, the Lewis acid is a hydrocarbylsilyl halide. More particularly the hydrocarbylsilyl halide is of the formula: R''_zSiX_{4-z}, wherein R''_z is alkyl C_{1-6}, aryl, X is halogen, z is an integer from 1 to 2. In one aspect R''_z is alkyl C_{1-6},more preferably methyl or ethyl. In another aspect, R''_z is aryl. Particularly preferred compounds are $MeSiCl_3$, Me_2SiCl_2, $EtSiCl_3$, Et_2SiCl_2, Ph-$SiCl_3$ and mixtures containing one or more of these compounds (wherein Me is methyl, Et is ethyl and Ph is phenyl group).

A further aspect is directed to products produced by the methods described above.

The hydrocarbylsilyl halide compounds advantageously are non-pyrophoric and thus easier to handle in promoting the carbonyl-ene reaction. The hydrocarbylsilyl halide are not moisture sensitive and can used when water is present as an impurity or generated in the reaction. Accordingly an aspect is to a method for preparing mono addition products in a carbonyl-ene reaction comprising conducting the carbony-ene reaction with a stoichiometric amount of a hydrocarbylsilyl halide of the formula: R''_zSiX_{4-z}, wherein R''_z is alkyl C_{1-6}, aryl, X is halogen, z is an integer from 1 to 2. In this regard, suitable enes are selected from alkenes having an allyic hydrogen, wherein suitable carbonyl enophiles have been described above. Thus a further aspect is directed to the use of a hydrocarbylsilyl halide as a Lewis acid. More particularly an aspect is directed to the use of a hydrocarbylsilyl halide of the formula above to promote a carbonyl-ene reaction.

In a second aspect, there is provided a method for making an alchohol-functionalized polyolefin from a Lewis acid promoted carbonyl ene reaction comprising

a. selecting a reactive polyisobutene having a number average molecular weight from about 1,000 to about 5000 and a methylvinylidene content greater than 50 mole percent;
b. selecting a carbonyl enophile;
c. selecting a Lewis acid; and
d. contacting step a), b) and c) under reactive conditions to form the polyolefin alcohol-functionalized polyolefin.

In a third aspect, there is provided a method for making an alcohol-functionalized polyolefin from a Lewis acid promoted carbonyl ene reaction comprising:

a. selecting a reactive polyisobutene having a number average molecular weight from about 700 to about 3,000 and a methylvinylidene content greater than 50 mole percent;
b. selecting a carbonyl enophile;
c. selecting a Lewis acid; and
d. contacting step a), b) and c) under reactive conditions to form the alcohol-functionalized polyolefin.

In a fourth aspect, there is provided a method for preparing mono addition products in a carbonyl-ene reaction comprising conducting the carbony-ene reaction with a stoichiometric amount of a hydrocarbylsilyl halide of the formula: R''_zSiX_{4-z}, wherein R''_z is alkyl C_{1-6}, aryl, X is halogen, z is an integer from 1 to 2.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, the terms used have the following meaning:

As used herein, unless otherwise specified the term "alkyl" means a straight chain or branched saturated hydrocarbon moiety. "Lower alkyl" means an alkyl group having 1 to 6 carbon atoms.

As used herein, unless otherwise specified the term "halogen" means fluorine, chlorine, bromine, or iodine.

As used herein, unless otherwise specified the term "haloalkyl" refers to an alkyl radical, as defined above, that is substituted by one or more halogen radicals, as defined above, e.g., trifluoromethyl, difluoromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 1-fluoromethyl-2-fluoroethyl, 3-bromo-2-fluoropropyl, 1-bromomethyl-2-bromoethyl, and the like.

As used herein, unless otherwise specified the term "acyl" means $-C(O)R^*$ where R^* is hydrogen, alkyl or aryl defined herein. The term "lower acyl" refers to where R^* is a lower alkyl defined above.