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(54) Title: METHOD OF NUCLEATING A POLYOLEFIN COMPOSITION WITH ACETAL-BASED COMPOUNDS

(57) Abstract: An acetal-based composition useful as a nucleating, gelling, thickening or clarifying agent is disclosed. The composition may be synthesized or provided in many different forms, including multicarbon diacetals formed from carbohydrates. Once synthesized, the compound may be employed as an additive in a plastic composition, such as (for example) a polypropylene copolymer. Co-additives may also be employed. Several aryl structures may reside upon the hydrocarbon chain backbone. One structure of such an acetal-based composition is a modified sorbitol with one or more aryl groups and at least one substituted group upon a terminal carbon in the chain.

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Cross-Reference to Related Applications

This application is a continuation in part (CIP) of an application entitled "Acetal-Based Compositions", filed April 26, 2004, application Serial Number 10/831,920.

Title of the Invention

METHOD OF NUCLEATING A POLYOLEFIN COMPOSITION WITH ACETAL-BASED COMPOUNDS

Background of the Invention

Derivatives of acetals of polyhydric alcohols are useful in several applications, including for example as nucleating agents for polymer resins, and as gelling and thickening agents for organic liquids. Dibenzylidene sorbitol type (DBS) compounds are known for use in such applications.

The use of nucleating agents to reduce the haze in articles manufactured from crystalline polyolefin resins is known in the art. Representative acetals of sorbitol and xylitol, which have been employed as clarifying agents, are described in several patents, including for example: Hamada, et al., United States Patent No. 4,016,118, dibenzylidene sorbitols; Kawai, et al., United States Patent No. 4,314,039, di(alkylbenzylidene) sorbitols; Mahaffey, Jr., United States Patent No. 4,371,645, di-acetals of sorbitol having at least one chlorine or bromine substituent; Kobayashi, et al., United States Patent No. 4,954,291, distribution of diacetals of sorbitol and xylitol made from a mixture of dimethyl or trimethyl substituted benzaldehyde and unsubstituted benzaldehyde. Another reference, United States Patent No. 5,049,605 to

Rekers et al. discloses bis(3,4-dialkylbenzylidene) sorbitols, including substituents forming a carbocyclic ring.

Substitution of various groups upon the benzyl ring portion(s) of DBS-based compounds may have a significant impact upon the suitability of such compounds as nucleating or clarifying agents. A significant amount of work in the past has been directed to modifying the substitution of the benzylidene ring substituent(s). However, efforts still are underway to develop other compounds that are likely to afford reduced haze (and corresponding greater clarity) when used as plastic additives in polymer compositions.

The chemical arts often are unpredictable. Changing any portion or substituted group in these particular types of compounds may have a significant impact upon the performance and utility of the compound. This invention recognizes important new compositions that have not been known before, and may be quite useful as plastic additives, or as gelling agents, thickeners, or for other purposes.

Detailed Description of the Invention

Reference now will be made to the embodiments of the invention, one or more examples of which are set forth below. Each example is provided by way of explanation of the invention, not as a limitation of the invention. It will be apparent to those skilled in the art that various modifications and variations can be made in this invention without departing from the scope or spirit of the invention.

A polyolefin additive composition is disclosed herein. In some applications, the polyolefin additive composition provides improved

transparency to plastic polymer compositions when added to such compositions. In some applications, the additive composition will be advantageous when used in connection with polypropylene, although various applications in connection with other polymers are within the scope of the invention.

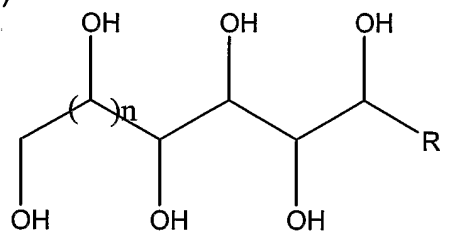
Olefin polymers which can be nucleated by such compositions (and whose transparency may be improved according to the practice of the invention) include polymers and copolymers of aliphatic mono-olefins containing from 2 to about 6 carbon atoms, which have an average molecular weight of from about 10,000 to about 2,000,000, preferably from about 30,000 to about 300,000, such as polyethylene, including linear low density polyethylene, low density polyethylene and high density polyethylene, polypropylene, crystalline ethylene/propylene copolymer (random or block), poly(1-butene) and polymethylpentene.

Examples of other thermoplastic polymer resins which may be nucleated with the disclosed acetal compounds include polyester, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) and polyamide, including nylon 6 and nylon 6,6, poly(phenylene sulfide), syndiotactic polystyrene and polyketones having carbonyl groups in their backbone.

The composition may comprise a polymer selected from aliphatic polyolefins and copolymers containing at least one aliphatic olefin and one or more ethylenically unsaturated comonomers and at least one mono-, di-, or tri-acetal of substituted alditol (such as allyl-sorbitol, propyl-sorbitol, allyl-xylitol, propyl-xylitol and the like).

The mono-, di-, or tri-acetal of substituted alditol may include a composition as described below. For example, and not by way of limitation, a substituted alditol as in Formula (I), which is combined with at least one mole of benzaldehyde selected from the compounds with Formula (II), as shown below.

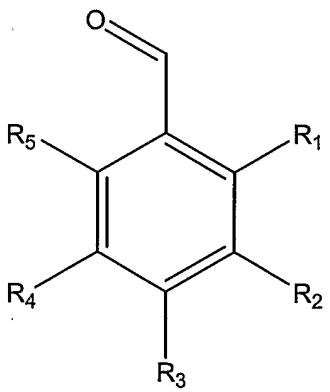
(I)



For Formula (I): n is 0, 1, or 2; and

R is independently selected from non-hydrogen groups including alkenyl groups (such as allyl), alkyl groups, alkoxy groups, hydroxyl alkyl groups, alkyl-halide groups.

(II)

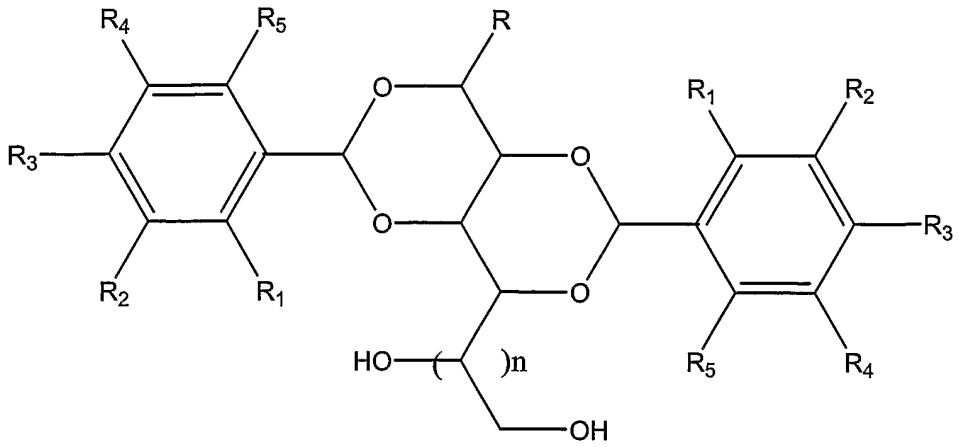


For Formula (II), R_1, R_2, R_3, R_4, and R_5 are independently selected from the group consisting of hydrogen, fluorocarbons, alkenyl, alkyl groups, alkynyl groups, alkoxy groups, carboxy groups, halides, and phenyl, or in some embodiments of the invention, any two adjacent groups may be combined to form a cyclic group, wherein said cyclic group may be comprised of methylenedioxy, cyclopentyl, cyclohexyl, or other similar cyclic groups.

An acetal compound may be formed in one particular embodiment of the invention by the process of: (a) reacting a polyhydric alcohol with an alkenyl molecule to form a first compound; and (b) reacting in a condensation reaction said first compound with an aromatic aldehyde to form an acetal compound. However, the invention may be practiced in other ways as well. The acetal compound thus formed may be a mono-, di-, or tri- acetal, but in many cases it has been found that a di-acetal is particularly useful. The acetal compound may comprise an allyl in one particular embodiment of the invention, as herein further described.

In some applications, such a reaction product or resulting composition is a di-acetal (and thus the result of a 1:2 molar ratio reaction between the alditol and benzaldehyde). A composition may be provided having the structure of Formula (III), below. A single acetal, or a triacetal, could also be provided in the practice of the invention, but one particular di-acetal composition is shown below:

(III)



In the composition, n may be 0, 1, or 2; and Ar_1 and Ar_2 are independently selected from substituted or unsubstituted aryl-containing groups. Furthermore, R may be selected from the group consisting of: alkenyls, alkyls, alkoxy, hydroxyl alkyls, and alkyl-halides. R may comprise an alkenyl, and in some particular embodiments of the invention, an allyl has been found to work quite well for the R group.

It should be appreciated that the R group stereochemistry is not defined, and the invention is not limited to any particular R group stereochemistry, such that all chemical structures provided herein shall cover any isomers that occur due to stereoisomers of the carbon atom to which R is attached.

It should be appreciated with regard to the composition set forth above that while only the 1,3; 2:4 isomer is represented (i.e. the numbered carbons on the sorbitol chain which form the two acetals), this structure is provided for convenience and illustration only and the invention is not

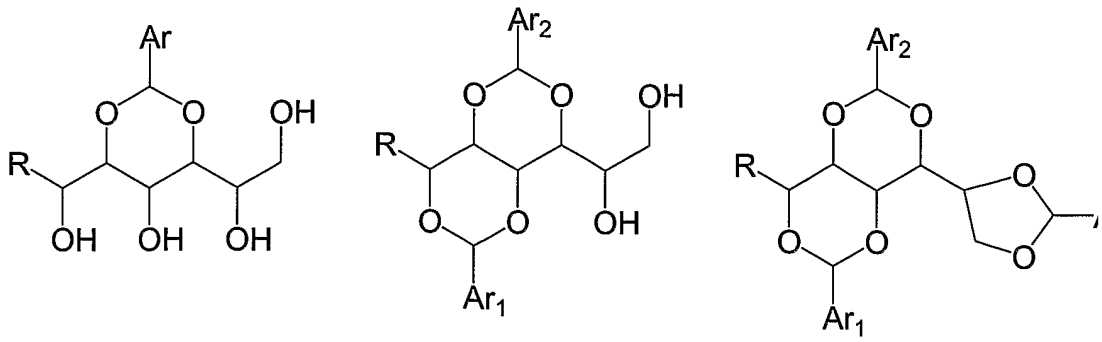
limited to only isomers of the 1,3: 2,4 type, but may include any and all other isomers as well, including also isomers of the 1:3; 4:6 and 2,4:3,5 type, as examples.

The diacetals, triacetals, and monoacetals of the invention may be condensation products of substituted alditols, such as (but not limited to) allyl-sorbitol, propyl-sorbitol, 1-methyl-2-propenyl sorbitol, allyl-xylitol, propyl-xylitol, and a (substituted) benzaldehyde. Examples of suitable (substituted) benzaldehydes include benzaldehyde, 4-ethylbenzaldehyde, 4-isobutylbenzaldehyde, 4-fluoro-3-methylbenzaldehyde, 5,6,7,8-tetrahydro-2-naphthaldehydebenzylidene, 3-methylbenzaldehyde, 4-propylbenzaldehyde, 4-butylbenzaldehyde, 4-methoxybenzaldehyde, 3-chlorobenzaldehyde, 3,4-dimethylbenzaldehyde, 3,5-difluorobenzaldehyde, 3-fluorobenzaldehyde, 4-fluorobenzaldehyde, 3-bromo-4-fluorobenzaldehyde, 3-methyl-4-methoxybenzaldehyde, 2,4,5-trimethylbenzaldehyde, 4-chloro-3-fluorobenzaldehyde, 4-methylbenzaldehyde, 3-bromobenzaldehyde, 4-methoxybenzaldehyde, 3,4-dichlorobenzaldehyde, 4-fluoro-3,5-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 4-bromobenzaldehyde, 3-ethoxybenzaldehyde, 4-allyloxybenzaldehyde, 3,5-dimethylbenzaldehyde, 4-chlorobenzaldehyde, 3-methoxybenzaldehyde, 4-(trifluoromethyl)benzaldehyde, 2-naphthaldehyde, 4-isopropylbenzaldehyde, 3,4-diethoxybenzaldehyde, 3-bromo-4-ethoxybenzaldehyde, piperonal, 3,4-dimethoxybenzaldehyde, 4-carboxybenzaldehyde, 3-hex-1-ynylbenzaldehyde, and 2-chlorobenzaldehyde. Preferred di-acetals of the present invention include 1,3:2,4-bis(4-ethylbenzylidene)-1-allyl-sorbitol, 1,3,2,4-bis(3'-methyl-4'-

fluoro-benzylidene)-1-propyl-sorbitol, 1,3,2,4-bis(5',6',7',8'-tetrahydro-2-naphthaldehydebenzylidene)-1-allyl-xylitol, bis-1,3,2-4-(3',4'-dimethylbenzylidene)-1"-methyl-2"-propyl-sorbitol, 1,3,2,4-bis(3',4'-dimethylbenzylidene)-1-propyl-xylitol.

The di-acetals and mono-acetals of the present invention may be prepared by a variety of techniques, some of which are known in the art. Generally, such procedures employ the reaction of one mole of substituted alditol (such as allyl-sorbitol, propyl-sorbitol, allyl-xylitol, propyl-xylitol and the like) with 2 moles of aldehyde (for diacetals), with 1 mole of aldehyde (for monoacetals), or with 3 moles of aldehyde (for triacetals) in the presence of an acid catalyst (inorganic acid such as hydrochloric acid or organic acid such as *p*-toluenesulfonic acid (pTSA)). Further, an organic solvent is employed that is miscible with water (such as low alkyl alcohols, *N-N*-dimethylformamide, or acetic acid) at room temperature.

In the practice of the invention, it is possible to have any number of DBS moities on the structure. It is common to have one, two, or three DBS (i.e. aryl-containing) moities on the hydrocarbon backbone. Below are several examples that can be employed in the method of nucleating a polyolefin composition. That is, one may employ one or more of the following:



wherein:

Ar, Ar_1 and Ar_2 are independently selected from substituted or unsubstituted aryl-containing groups; and

R is selected from the group consisting of: alkenyls, alkyls, alkoxy, hydroxyl alkyls, alkyl-halides and derivatives thereof.

Also, co-additives may be combined with said polyolefin composition. Examples of co-additives that can be used are set forth below in (1) - (3). Example 21 below shows yet another example of a co-additives lauryl sulfuric acid Na, that may be employed. Many other examples could be employed, and the co-additives below could be used with essentially any of the nucleating agent structures or compositions disclosed herein. Also, more than one co-additive set forth below could be employed, and the amount or concentrion employed would vary for a given application.

(1) Co-additives for inhibiting migration of odor and taste.

Alkali metal salts of amino acids (at least one amino acid chosen from the following: glycine, L-alanine, L-phenyl-alanine, L-isoleucine, L-valine, L-leucine, L-proline, L-arginine, L-asparatic acid, L-cystine, L-glutamic acid, L-serine, L- histidine, L-tryptophan, L-lysine, L-threonine, L-methionine, DL-ethionine, L-cysteine, L-tyrosine, L-asparagine, L-glutamine, L-norvaline, and L-a-amino butyric acid.) and 0.1 to 100 parts by weight of at least one fatty acid with 8-32 carbon atoms (octane acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxy stearic acid, behenic acid, montan acid, oleic acid, linoleic acid, ereo-stearic acid, ricinoleic acid, and erucic acid).

(2) Co-additives for inhibiting migration of odor and taste and depression the melting point of DBS: A: At least a saturated or unsaturated aliphatic alcohol with 6-32 carbon atoms (for example: lauric alcohol). B: and at least a saturated or unsaturated aliphaltic carboxylic acid with 8-32 carbon atoms having at least one hydroxy group within the molecule (for example: 12-hydroxy stearic acid), C: at least one type chosen from the following groups: lithium salt, sodium salt, or potassium salt of a saturated or unsaturated fatty acid with 8-32 carbon atoms that may have at least one hydroxyl group within the molecule, or D: at least one type sulfuric acid ester salt chosen from the following group: lauryl sulfuric

acid salt, stearyl sulfuric acid salt, oleyl sulfuric acid salt, and polyoxyethylene stearyl ether sulfuric acid salts.

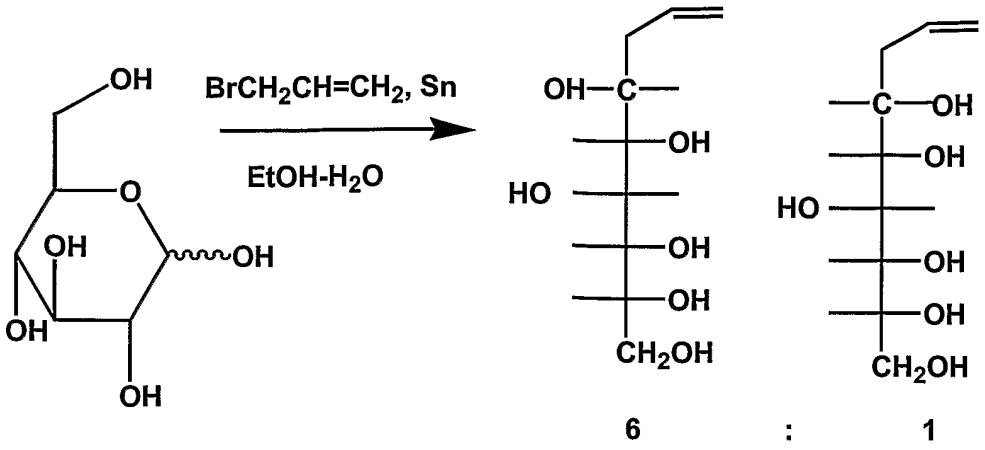
(3) Co-Additives having a granular or powdery diacetal composition; wherein the binder is selected from the group consisting of monocarboxylic acids, polycarboxylic acids, partial salts of polycarboxylic acids, esters of phosphoric acid and at least one member selected from the group consisting of C1-C30 monohydric aliphatic alcohols and C2-C30 polyhydric aliphatic alcohols, esters of phosphorous acid and at least-one member selected from the group consisting of C1-C30 monohydric aliphatic alcohols and C2-C30 polyhydric aliphatic alcohols, esters of phosphoric acid and at least one member selected from the group consisting of C6-C30 monohydric aromatic alcohols and C6-C30 polyhydric aromatic alcohols, esters of phosphorous acid and at least one member selected from the group consisting of C6-C30 monohydric aromatic alcohols and C6-C30 polyhydric aromatic alcohols, taurine, salts of sulfuric acid ester, sulfonic acid salts, salts of phosphoric acid ester and mono-, di- and tri(C6-C30 fatty acid) aluminum salts, each of which may have, in the molecule, at least one bond or functional group selected from the group consisting of an ether bond, an ester bond, a thioether bond, an amide bond, a halogen atom, amino group, hydroxyl groups, a heterocyclic group and carbonyl group.

Synthesis Methods for Di-Acetals

One method that can be employed to prepare di-acetals of the invention is described in United States Patent No. 5,106,999 to Gardlik et al., which is hereby incorporated by reference.

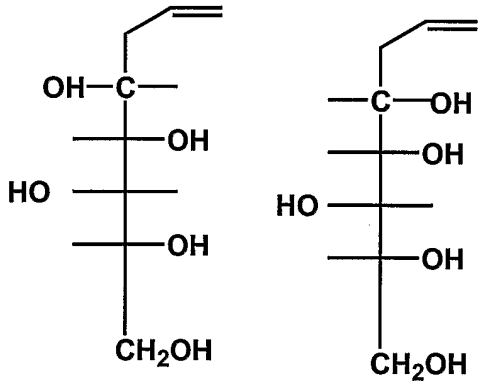
Methods to prepare and synthesize the carbohydrates of varying chain length are disclosed in Kim, Gordon, Schmid, and Whitesides, *Tin and Indium Mediated Allylation in Aqueous Media: Application to Unprotected Carbohydrates*, J. Org. Chem, 5500-5507, 58 (1993) and in Whiteside, *Journal of the American Chemical Society*, 113, 6674-6675 (1991). Whiteside has suggested the reaction of glucose with allyl bromide/tin.

One reaction method that may be employed in the preparing starting materials for the synthesis of compositions needed in the practice of the invention are shown below, in which an allyl group may be added to a carbohydrate. The reaction scheme illustrated is merely one example, and similar reactions can be carried out for carbohydrates having more or less carbon groups in the chain.



1,2,3-trideoxy-D-glycero-D-ido-nonenitol

1,2,3-trideoxy-D-glycero-D-gulo-nonenitol



1,2,3-trideoxy-D-ido-octenitol

1,2,3-trideoxy-D-gulo-octenitol

In the practice of the invention, an acetal compound formed by the process of: (a) reacting a carbohydrate and an alkenyl group to form a first compound; and (b) reacting in a condensation reaction said first compound with an aromatic aldehyde to form an acetal compound. In some applications, the alkenyl group comprises an allyl.

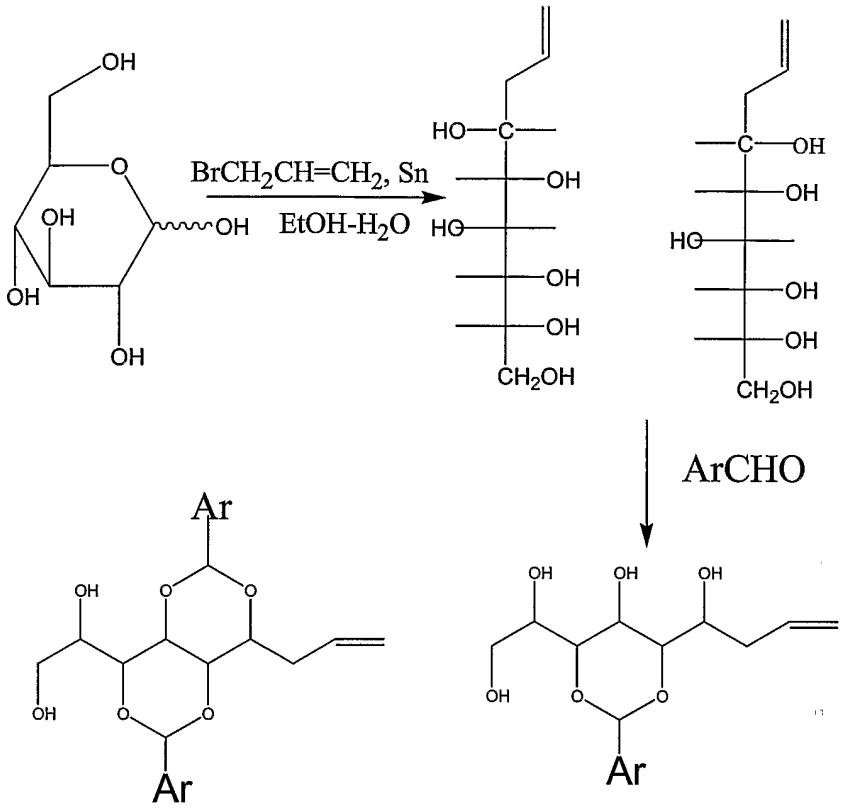
It has been discovered in the course of work leading to one embodiment of the invention herein that allyl bromide/tin chemistry as illustrated above is one manner of synthesis for a carbohydrate hydrocarbon chain that can be used as one step in a sequence of reactions to unexpectedly provide significant advantages and valuable compositions. This general reaction pathway may be used in various forms to synthesize carbohydrates in the manufacture of the compositions of the invention. One embodiment of the invention relates to the use of carbohydrate synthesis reactions in combination with other acetal formation reactions to prepare compositions of the invention.

Substituted sorbitol diacetals, triacetals, and monoacetals may be prepared. These structures contain mixtures of any correlated types of acetals (such as the related di-, tri-, and/or mono-acetals of the target acetal). Although it may not always be necessary to remove these impurities (particularly if they are present in very low proportions) prior to incorporation of the di-acetal, triacetal or monoacetal into the target polyolefin, it may be desirable to do so and such purification may serve to enhance the transparency of the resin produced thereby.

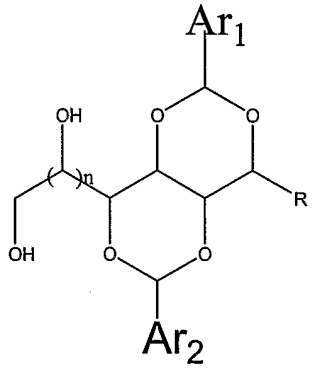
Purification of a di-acetal may be accomplished, in one embodiment of the invention, by removal of any present tri-acetals by the extraction thereof with a relatively non-polar solvent. As one non-limited example, by removal of the impurities, the product may be purified so that the amount of di-acetal in the additive composition contains at least about 95 percent and even up to 98 percent di-acetal or more, depending upon the application.

A more complete synthesis pathway is shown below, which is merely illustrative, and not limited to only those species or reactions shown:

Synthesis Pathway(s)



Generic Structure of a Synthesized Acetal-based Composition



Many different substituted benzyl groups may be employed for Ar_1 and Ar_2 in the practice of the invention, as shown by several representative examples in Table 1, which were synthesized and tested as shown in the Examples listed herein. Substituted groups for Ar_1 and/or Ar_2 are not limited to only those found in Table 1. For example, Table 1 reports various compositions for which n= 0 and where n=1 for various substituted Ar_1 and Ar_2 groups. When n = 0, the xylitol moity is employed. When n = 1, the sorbitol moity is employed. Although n = 2 compounds are not reported in Table 1, such compounds are within the scope of the invention, and are within the teachings provided herein. There is no practical limit to what may be substituted in such compositions, so long as they are chemically possible. However, it has been found that certain substituted groups on this compound provide enhanced properties.

In the practice of the invention, R may be selected from a wide variety of compounds, including without limitation and by way of example:

$-CH_3$; $-CH_2CH_3$;

-CH2CH2CH3; $-CH_2CH_2CH_2CH_3$;

$-CH_2CH{=}CH_2$; $-CH(CH_3)CH{=}CH_2$;

$-CH_2CH$-X-CH_2-X' ; $-CH_2CH_2$-X''-CH_2-CH_3 ;

$-CH_2CH$-X'''-CH_2OH; -CH-OH-CH-OH-CH_2-OH.

With regard to the compounds above, X, X', X'' , and X''' comprise independently selected halide groups in those selected compounds, if they are employed.

The allyl species ($-CH_2CH{=}CH_2$) is sometimes particularly advantageous, and several such species were synthesized and reported along with others in Table 1 herein.

Table 1: Substitution of Groups with Corresponding Melting Points

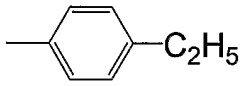
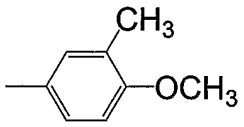
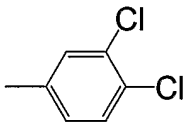
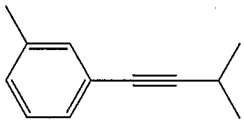
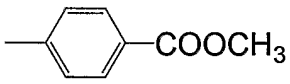
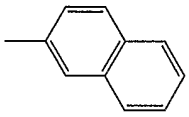
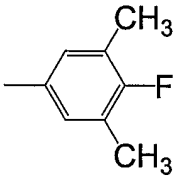
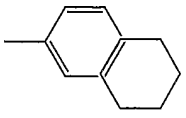
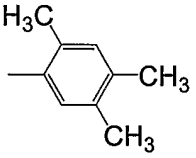
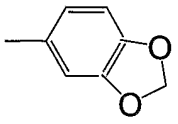
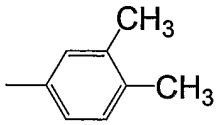
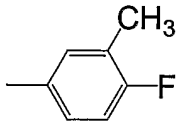
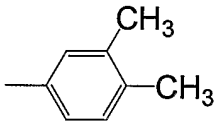
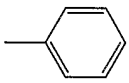
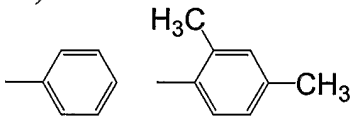
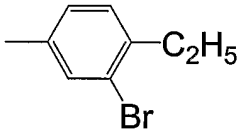
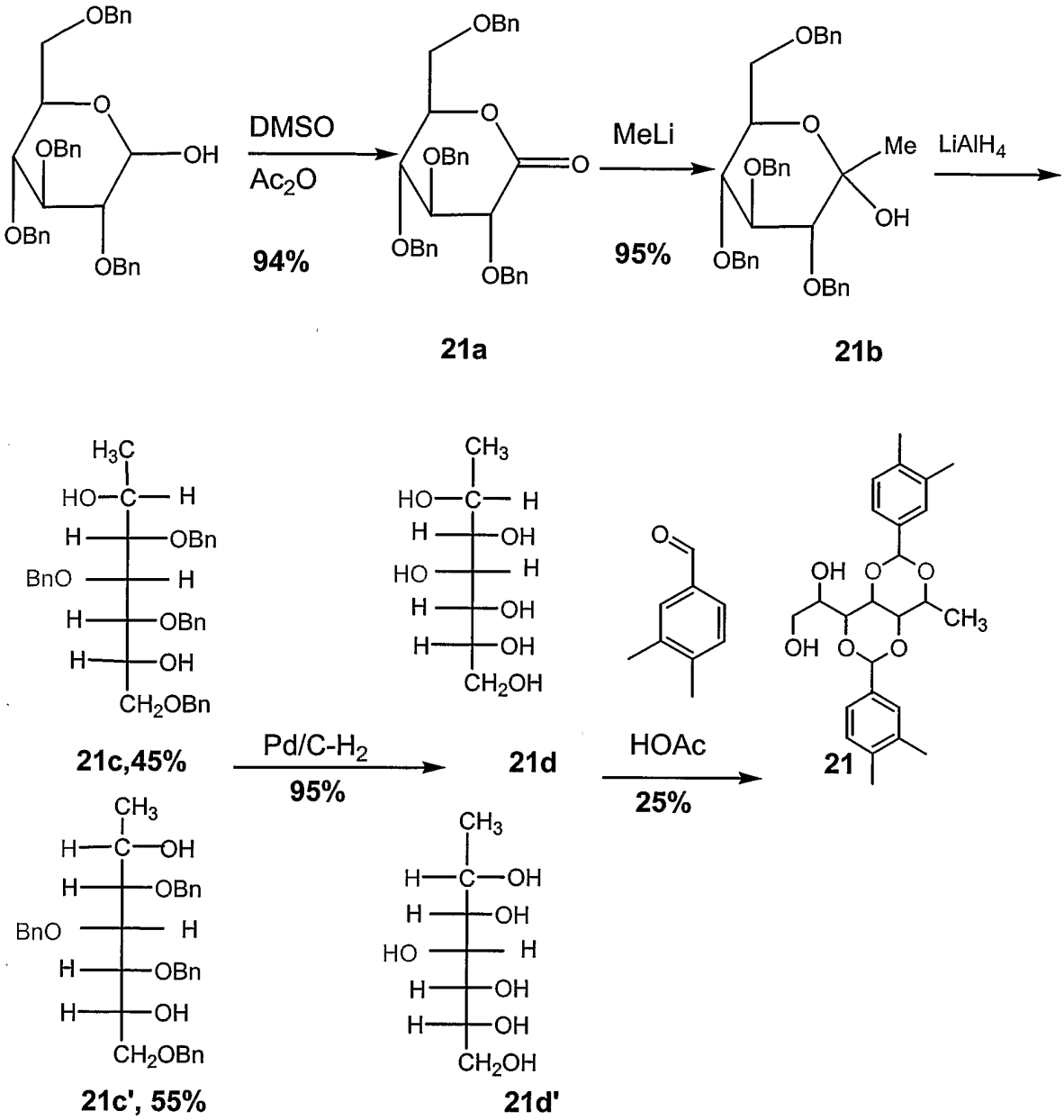
Example Reported Herein	n	R	Ar_1, Ar_2	Melting Point (°C)
2	1	$-CH_2CH=CH_2$		244-246
3	1	$-CH_2CH=CH_2$		237-239
4	1	$-CH_2CH=CH_2$		275-280
5	1	$-CH_2CH=CH_2$		190-192
6	1	$-CH_2CH=CH_2$		295-300
7	1	$-CH_2CH=CH_2$		247-249
8	1	$-CH_2CH=CH_2$		286-288
10	0	$-CH_2CH=CH_2$		210-212
11	0	$-CH_2CH=CH_2$		274-276

Table 1 (continued)

Example Reported Herein	n	R	Ar_1, Ar_2	Melting Point (°C)
12	0	$-CH_2CH=CH_2$		217-219
13	0	$-CH_2CH_2CH_3$		255-257
14	1	$-CH_2CH_2CH_3$		252-254
15	1	$-CH(CH_3)CH=CH_2$		233-235
16	1	$-CH_2CHBrCH_2Br$ (90%) $-CH_2CHBrCH_2OH$ (10%)		188-190
17	1	$-CH_2CH=CH_2$		234-236
19a	1	$-CH_2CH=CH_2$		268-269

Synthesis of Example 21



Example 1
1-Allyl Sorbitol

A 3L, three-necked round bottom flask, equipped with heating mantle, stirrer, nitrogen inlet, and condensor, was charged with 900 mL of ethanol, 150 mL of water, 180 g (1.00 mole) of D-glucose, 119 g (1.00 mole) of tin powder (-100 mesh), and 121 g (1.00 mole) of allyl bromide. The mixture was stirred and slowly heated to reflux – a significant exotherm and gas evolution was observed at 60°C. The gray suspension was stirred at reflux for two days, in which time the reaction mixture turned an orange/brown color. Heat was removed and the mixture was allowed to cool to room temperature. The reaction was neutralized to pH = 7 by adding approximately 200 ml of 5M NaOH aqueous solution. The suspension was filtered to remove solids, and the yellow solution was decolorized with multiple treatments of activated carbon. The activated carbon was removed by filtration, and the solvent was removed by rotary evaporation to isolate a white syrup. Typical yield was 200g with threo-erythro ratio of 1:6, based on GC-MS. The syrup was used without further purification.

Pure erythro isomer could be obtained by hydrolysis of any of the example **2-8**. ^{1}H NMR (500 MHz, D_2O, ppm): 2.34-2.37 (m, 2H), 3.63-3.95 (m, 7H), 5.13-5.20 (m, 2H), 5.88-5.89 (m, 1H). ^{13}C NMR (125 MHz, D_2O, ppm): 38.32, 63.69, 70.74, 71.14, 71.80, 71.92, 74.58, 118.60, 135.72.

Example 2
Bis-1,3: 2,4-(4'-ethylbenzylidene) 1-Allyl Sorbitol

A 2L reaction kettle, equipped with a stirrer and nitrogen inlet, was charged with 111 g (0.50 mol) of 1-allyl sorbitol syrup (product of **Example 1**) in 100 mL of 6N HCl solution. 134 g (1.0 mol) of 4-ethylbenzaldehyde in 800 mL of methanol was added to the reaction vessel. The clear solution was stirred for 48 hours, during which time a significant amount of white precipitate formed. The powder was isolated by filtration and washed with 250 ml of 1M NaOH aqueous solution. The powder was suspended in water and further neutralized to pH = 7 with a small amount of NaOH. The suspension was heated to boiling, then filtered. The white powder was washed with 7 x 500 ml of boiling water. The washed powder dried overnight. The powder was then stirred in 500 mL of cyclohexane, heated until boiling, filtered, and washed with 2 x 250 ml of boiling cyclohexane. The isolated white powder was dried in a vacuum oven to give 107 g of product, m.p. 244-246°C. The purity was above 99%, based on GC-MS. 1H NMR(300 MHz, DMSO-d_6, ppm): 1.14-1.19 (t, 6H), 2.39-2.44 (t, 2H), 2.56-2.63 (q, 4H), 3.41-4.10 (m, 7H), 4.38-4.42 (t, 1H), 4.81-4.83 (d, 1H), 5.07-5.19 (q, 2H), 5.60-5.64 (d, 2H), 5.84-5.89 (m, 1H), 7.19-7.23 (t, 4H), 7.34-7.38 (t, 4H).

Examples 3-8

A variety of allyl-substituted dibenzylidene-based (DBS) molecules were synthesized using the procedures similar to the one described in **Example 2** above. Structures are shown in Table I, with measured values

for melting point. All derivatives had NMR consistent with the indicated structures, and purities of at least 95%, based on GC-MS.

Example 9
1-Allyl Xylitol

A 5L three-necked round bottom flask, equipped with heating mantle, stirrer, nitrogen inlet, and condenser, was charged with 1.8 liters of ethanol, 0.3 liters of water, 300 g (2.00 mole) of D-xylose, 242 g (2.04 mole) of tin powder (-325 mesh), and 242 g (2.00 mole) of allyl bromide. The mixture was stirred and slowly heated to reflux – a significant exotherm and gas evolution was observed at 60°C. The gray suspension was stirred at reflux for three days, in which time the reaction mixture turned an orange/brown color. Heat was removed and the mixture was allowed to cool to room temperature. The reaction was neutralized to pH = 7 by adding approximately 400 ml of 5M NaOH aqueous solution. The suspension was filtered to remove solids, and the yellow solution was decolorized with multiple treatments of activated carbon. The activated carbon was removed by filtration, and the solvent was removed by rotary evaporation to isolate a white syrup. Typical yield was 320g. 1H NMR(300 MHz, D_2O, ppm): 2.33-2.39 (m, 2H), 3.55-3.89 (m, 6H), 5.14-5.23 (m, 2H), 5.89 (m, 1H). The syrup was used without further purification.

Example 10
Bis-1,3:2,4-(5',6',7',8'-tetrahydro-2-naphthaldehydebenzylidene) 1-Allyl Xylitol

A two liter reaction kettle, equipped with a stirrer and nitrogen inlet, was charged with 144 g (0.75 mol) of 1-allyl xylitol syrup (product of example 9), 300 mL of water, and 100 mL of concentrated (12N) HCl. The mixture was stirred until the 1-allyl xylitol had completely dissolved. 240 g (1.50 mol) of 5',6',7',8'-tetrahydro-2-naphthaldehyde in 400 mL of methanol was added to the reaction vessel. The solution was stirred for two days, during which time a significant amount of white precipitate formed. The powder was isolated by filtration and washed with 250 ml of 1M NaOH aqueous solution. The powder was suspended in water and further neutralized to pH = 8 with a small amount of NaOH. The suspension was heated to boiling, then filtered. The white powder was washed with 7 x 500 ml of boiling water. The washed powder dried overnight. The powder was then stirred in 0.5 liters of cyclohexane, heated until boiling, filtered, and washed with 2 x 250 ml of boiling cyclohexane. The isolated white powder was dried in a vacuum oven, to give 47.8 g of product, m.p. 210-212°C. The purity was 99%, based on GC-MS. 1H NMR (300 MHz, DMSO-d_6, ppm): 1.72 (m, 8H), 2.36-2.51 (t, 2H), 2.71 (m, 8H), 3.54-4.03 (m, 6H), 4.76-4.80 (t, 1H), 5.07-5.17 (q, 2H), 5.56-5.77 (d, 2H), 5.80-5.90 (m, 1H), 7.02-7.06 (m, 2H), 7.11-7.17 (m, 4H).

Example 11, 12

A variety of allyl DBXs were synthesized using the procedure similar to the one described in Example 2. The structures of example 10 and 11 are shown in Table 1. All derivatives had NMR consistent with the indicated structures, and purities of at least 95%, based on GC-MS.

Example 13
Bis-1,3:2,4-(3',4'-Dimethylbenzylidene) 1-Propyl Xylitol

58 g (0.3 mol) of 1-allyl xylitol syrup (**Example 8**) was dissolved in 60 ml water. About 0.6 g of platinum (5% weight on activated carbon) was added and the mixture was hydrogenated at room temperature with hydrogen pressure at 60 psi. The reaction was stopped until no hydrogen pressure drop was observed. The solid was filtered. The allyl group of the solution was completely turned into propyl group based on NMR. 100g (0.6 mol) of 3,4-dimethyl benzaldehyde, 500 ml ethanol, and 50 mL concentrated HCl (12N) were added into the sugar solution. The clear solution was stirred at room temperature overnight, during which time a significant amount of white precipitate formed. The powder was isolated by filtration and washed with 100 ml of 1M NaOH aqueous solution. The powder was suspended in water and further neutralized to pH = 7 with a small amount of NaOH. The suspension was heated to boiling, then filtered. The white powder was washed with 7 x 500 ml of boiling water. The washed powder dried overnight. The powder was then stirred in 500 mL of cyclohexane, heated until boiling, filtered, and washed with 2 x 250 ml of boiling cyclohexane. The isolated white powder was washed with

methanol, dried in a vacuum oven to give 21 g of product, m.p. 255-257°C. The purity was above 98%, based on GC-MS. 1H NMR(300 MHz, DMSO-d_6, ppm): 0.89-0.93 (t, 3H), 1.30-1.50 (m, 2H), 1.50-1.70 (m, 2H), 2.22 (12H), 3.50-4.05 (m, 6H), 4.78 (1H), 5.56-5.59 (d, 2H), 7.14-7.21 (m, 6H).

Example 14
Bis-1,3:2,4-(3'-methyl-4'-fluoro-benzylidene) 1-Propyl Sorbitol

About 85 g (0.38 mol) of 1-allyl sorbitol syrup (product of example 1) was dissolved in 85 ml water. 0.8 g of platinum (5% weight on activated carbon) was added and the mixture was hydrogenated at room temperature with hydrogen pressure at 60 psi. The reaction was stopped until no hydrogen pressure drop was observed. The solid was filtered. The allyl group of the solution was completely turned into propyl group based on NMR.

75g (0.54 mol) of 3-methyl-4-fluoro benzaldehyde, 500 ml ethanol, and 56 mL concentrated HCl (12N) were added into the sugar solution. The clear solution was stirred at room temperature overnight, during which time a significant amount of white precipitate formed. The powder was isolated by filtration and washed with 100 ml of 1M NaOH aqueous solution. The powder was suspended in water and further neutralized to pH = 7 with a small amount of NaOH. The suspension was heated to boiling, then filtered. The white powder was washed with 7 x 500 ml of boiling water. The washed powder dried overnight. The powder was then stirred in 500 mL of cyclohexane, heated until boiling, filtered, and washed with 2 x 250 ml of boiling cyclohexane. The isolated white powder was washed with methanol, dried in a vacuum oven to give 21 g of product, m.p. 253°C. The

purity was above 98%, based on GC-MS. 1H NMR(300 MHz, DMSO-d_6, ppm): 0.91-0.95 (t, 3H), 1.40-1.48 (m, 2H), 1.54-1.67 (m, 2H), 2.13-2.25 (6H), 3.42-4.05 (m, 7H), 4.40 (t,1H), 4.82-4.84 (d, 1H), 5.60-5.62 (d, 2H), 7.11-7.16 (m, 2H), 7.30-7.37 (m, 4H).

Example 15
Bis-1,3:2,4-(3',4'-Dimethylbenzylidene) 1'-Methyl-2'-PropenylSorbitol

A two liter three-necked round bottom flask, equipped with heating mantle, stirrer, nitrogen inlet, and a condensor, was charged with 600 mL of ethanol, 100 mL of water, 126 g (0.70 mole) of D-glucose, 84 g (0.7 mole) of tin powder (-100 mesh), and 131 g (0.97 mole) of crotyl bromide. The mixture was stirred and slowly heated to reflux – a significant exotherm and gas evolution was observed at 60°C. The gray suspension was stirred at reflux overnight, in which time the reaction mixture turned light yellow. Heat was removed and the mixture was allowed to cool to room temperature. The reaction was filtrated and the solution was stirred with 188 g (1.4 mol) 3,4-dimethyl benzaldehyde overnight, during which time a significant amount of precipitate formed. The yellow solid was isolated by filtration, washed with methanol to give a white powder, m.p. 233-235°C. GC-MS and NMR indicated the desired compound as a mixture of two diastereomers (2:1), of 1-methyl-2-propenyl.

Example 16
Bis-1,3,2,4-Dibenzylidene 2',3'-Dibromopropyl Sorbitol/ Bis-1,3,2,4-Dibenzylidene 2'-Bromo-3'-Hydroxypropyl Sorbitol

An aqueous solution of 90 g allyl sorbitol syrup (**Example 1**) in 110 g of methanol was titrated with bromine until a light yellow solution. Small amount of $NaHSO_3$ was added to give a colorless solution. 1.9 g of p-toulenesulfonic acid monohydrate was added. The clear solution was stirred overnight, during which time a significant amount of white precipitate formed. The powder was isolated by filtration and washed with 1M NaOH aqueous solution. The powder was suspended in water and further neutralized to pH = 7 with a small amount of NaOH. The suspension was heated to boiling, then filtered. The white powder was washed with 7 x 500 ml of boiling water. The washed powder dried overnight. The powder was then stirred in 50 mL of cyclohexane, heated until boiling, filtered, and washed with 2 x 25 ml of boiling cyclohexane. The product was dried in a vacuum oven to give 7.3 g of white powder, m.p. 188-190°C. GC-MS and NMR indicated a mixture of bis-1,3:2,4-dibenzylidene 2',3'-dibromopropyl sorbitol (90%) and bis-1,3:2,4-dibenzylidene 2'-bromo-3'-hydroxypropyl sorbitol (10%).

Example 17
Asymmetric benzylidene/2,4-dimethylbenzylidene 1-Allyl Sorbitol

A 2L reaction kettle, equipped with a stirrer and nitrogen inlet, was charged with 111 g (0.50 mol) of 1-allyl sorbitol syrup (product of **Example 1**) in 280 ml methanol solution. 9.5 g of pTSA, 53 g (0.5 mol) of benzaldehyde and 67 g (0.50 mol) of 2,4-dimethylbenzaldehyde were

added to the reaction vessel. The clear solution was stirred for 48 hours, during which time a significant amount of white precipitate formed. The powder was isolated by filtration and washed with 250 ml of 1M NaOH aqueous solution. The powder was suspended in water and further neutralized to pH = 7 with a small amount of NaOH. The suspension was heated to boiling, then filtered. The white powder was washed with 7 x 500 ml of boiling water. The washed powder dried overnight. The powder was then stirred in 500 mL of cyclohexane, heated until boiling, filtered, and washed with 2 x 250 ml of boiling cyclohexane. The isolated white powder was dried in a vacuum oven to give 38.4 g of product, m.p. 234-236°C. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(benzylidene):2,4-O-(2,4-dimethylbenzylidene) 1-allyl sorbitol and 1,3-O-(2,4-dimethylbenzylidene):2,4-O-benzylidene 1-allyl sorbitol (85%), 1,3:2,4-bis(benzylidene) 1-allyl sorbitol (5%) and 1,3:2,4-bis(2,4-dimethylbenzylidene) 1-allyl sorbitol (10%).

Example 18
Tri-1,3:2,4:5,6-benzylidene-1-Allyl Sorbitol

111 g (0.50 mol) of 1-allyl sorbitol syrup (product of **Example 1**) was dissolved in 111 g of water. The solution was mixed with 50 g of ice. With an ice cooling bath, 90 mL of 93% of sulfuric acid was added slowly so the temperature was below 20°C. 106 g (1.0 mol) of benzaldehyde was added. A dark pink suspension was formed. The reaction was allowed to stand at room temperature overnight. The resultant yellow solid was collected by filtration, neutralized with 10% NaOH solution. The solid was washed with boiling

water, then cool methanol to give a white solid with mp of 216-218°C. Two diastereomers (differ only at the methane carbon attached to the oxygen atoms on carbon 5 and 6 of the allyl sorbitol moiety. The methane carbon can either be in the R or S conformation) with ratio 24:76 were detected by GC-MS. ^{1}H NMR(500 MHz, DMSO-*d6*, ppm): 2.43-2.45 (t, 2H), 3.95-4.52 (m, 7H), 5.10-5.20 (dd, 2H), 5.72 (s, 1H), 5.79 (s, 1H), 5.89 (s, 1H), 5.86-5.92 (m, 1H), 7.36-7.50 (m, 15H). ^{13}C NMR(125 MHz, DMSO-d_6, ppm): 34.2, 67.0, 69.6, 70.3, 73.3, 76.9, 77.6, 99.0, 99.1, 102.8, 109.3, 117.6, 126.0, 126.6, 128.0, 128.1, 128.2, 128.6, 128.7, 129.2, 134.0, 137.8, 138.2, 138.4.

Example 19
Bis-1,3: 2,4-(3'-bromo-4'-ethylbenzylidene)-1-Allyl Sorbitol/ Mono 2, 4-(3'-bromo-4'-ethylbenzylidene)-1-Allyl Sorbitol

A one liter 3-Neck flask, equipped with a mechanical stirring motor, glass stopper, and gas inlet; was purged with argon for 10 minutes. To this vessel, was added 335.2 mL of a 0.4M methanolic solution of 1-allyl sorbitol (30.07g, 134.1 mmol) (product of example 1) and 60.00g (281.6 mmol) of 3-bromo-4-ethylbenzaldehyde. After stirring reactants for 10 minutes, 42 mL of HCl (12M) was added to catalyze the reaction. Within two minutes following HCl addition, formation of a precipitate occurred and the solution began to take on a pinkish hue. After 3h of reaction, the pinkish tint has dissipated greatly and the amount of pinkish-white solids had increased. The contents were stirred rapidly and reaction progress was monitored by GC/MS every 8-12 hours. After 48h, during which a significant amount of off-white precipitate had formed, the reaction was quenched with 54.00g (962.5 mmol) postassium hydroxide [pre-dissolved in D.I. H_2O], thereby,

giving the mixture a final pH of 12-13. The crude solids were isolated by Buchner funnel vacuum filtration and washed with 800 ml of boiling D.I. H_2O. To remove unreacted sugar, the material was dried overnight, ground to a fine powder, and suspended in 1000 mL of D.I. H_2O. The slurried mixture was brought to a boil and stirred for 30 minutes. The solids were captured via Buchner funnel filtration and further washed with boiling D.I. H_2O (3 x 1000 mL). To remove residual aldehyde, the aforementioned procedure was repeated utilizing boiling methanol as wash solvent. After drying overnight, GC/MS of the solid material showed a mixture of mono:di benzylidene sorbitols [36.85g; 44.5% crude yield]. To separate this mixture, the crude, white solid was ground to a fine powder, stirred in a boiling 50:50 solvent mixture (CH_3OH : D.I. H_2O) for 1 h, hot filtered via Buchner funnel filtration and vacuum dried to give 27.99g of a soft, white powder [33.8% isolated yield of the DBS]. Analytical examination revealed this material to be **(19a) Bis-1,3, 2,4-(3'-bromo-4'-ethylbenzylidene)-1-allylsorbitol** [see below]. Upon standing overnight, a gelled, white precipitate was observed in the wash solvent utilized during final purification of the DBS [50:50; CH_3OH : D.I. H_2O]. This precipitate was isolated via Buchner funnel vacuum filtration and vacuum dried to yield 7.48g of a white solid [MBS]. Analytical analysis elucidated this material as **(19b) Mono 2, 4-(3'-bromo-4'-ethylbenzylidene)-1-allylsorbitol** [see below].

(19a) Analytical results found for **Bis-1,3, 2,4-(3'-bromo-4'-ethylbenzylidene)-1-allylsorbitol** [$C_{27}H_{32}O_6Br_2$]: The isolated white powder was dried in a vacuum oven (<10^{-1} mm Hg) at 90°C for 18h to give 27.99 g of a soft, white powder, m.p. 268.2-268.6°C [under argon]. Purity

was >98.3% based on GC-MS. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 1.15 (dt, 6H, –$CH_2C\underline{H}_3$); 2.42 (tdd, 2H, -allylic methylene); 2.70 (dq, 4H, –$C\underline{H}_2CH_3$); 3.44 (b, m, 1H); 3.61 (b, dq, 1H); 3.74 (b, m, 1H); 3.84 (b, d, 2H); 4.10 (b, m, 2H); 4.43 (t, 1H, 2° –OH); 4.90 (d, 1H, 1° –OH); 5.14 (b, qm, 2H, –$CH=C\underline{H}_2$); 5.63 (s, 1H, acetal); 5.67 (s, 1H, acetal) 5.88 (m, 1H, –$C\underline{H}=CH_2$); 7.38 (b, m, 4H, aromatic); 7.58 (b, s, 1H, aromatic) 7.62 (b, d, 1H, aromatic). ^{13}C NMR (500 MHz, DMSO-d_6, δ ppm): 14.25 (–$CH_2\underline{C}H_3$); 28.50 (–$\underline{C}H_2CH_3$); 34.29 (-allylic); 62.60; 67.73; 68.86; 70.84; 77.03; 77.53; 97.83 (acetal); 97.94 (acetal); 117.49 (–$CH=\underline{C}H_2$); 122.81; 122.88; 125.64; 125.78; 129.49; 129.62; 129.72; 129.89; 134.13 (–$\underline{C}H=CH_2$); 138.33; 138.45; 142.91; 142.97.

(19b) Analytical results found for **Mono-2, 4-(3'-bromo-4'-ethylbenzylidene)-1-allylsorbitol** [$C_{18}H_{25}O_6Br$]: The isolated white powder was dried in a vacuum oven (<10^{-1} mm Hg) at 70°C for 18h to give 7.58 g of a soft, white powder, m.p. 199.8-200.5°C [under argon]. Purity was >96% [contained < 4% DBS], based on GC-MS. ^{1}H NMR (500 MHz, DMSO-d_6, δ ppm): 1.16 (t, 3H, –$CH_2C\underline{H}_3$); 2.10 (m, 1H, -allylic methylene); 2.40 (b, m, 1H, -allylic methylene); 2.70 (q, 2H, –$C\underline{H}_2CH_3$); 3.41 (m, 1H); 3.47 (b, d, 1H); 3.57 (b, m, 1H); 3.62 (b, d, 1H); 3.74 (b, dm, 2H); 3.88 (b, d, 1H); 4.34 (d, 1H, 1° –OH); 4.40 (t, 1H, 2° –OH); 4.70 (d, 1H, 1° –OH); 4.78 (d, 1H, 1° –OH); 5.03 (b, m, 2H, –$CH=C\underline{H}_2$); 5.50 (s, 1H, acetal); 5.91 (b, m, 1H, –$C\underline{H}=CH_2$); 7.36 (b, m, 2H, aromatic); 7.67 (b, d, 1H, aromatic). ^{13}C NMR (500 MHz, DMSO-d_6, δ ppm): 14.26 (–$CH_2\underline{C}H_3$); 28.49 (–$\underline{C}H_2CH_3$); 37.89 (-allylic); 60.51; 62.70; 67.15; 69.15; 79.54; 82.33; 98.84 (acetal); 116.33 (–

CH=CH$_2$); 122.88; 125.99; 129.42; 130.10; 135.92 (–CH=CH$_2$); 138.56; 142.87.

Example 20
Mixture of Bis-1,3:2,4-(4'-ethylbenzylidene) 1-Allyl Sorbitol, 12-Hydroxy Stearic Acid, and Lauryl Sulfuric Acid Na

In a clean 250 ml one-neck flask with a stir bar, was charged with 9.50 g of Bis-1,3;2,4-(4'-ethylbenzylidene) 1-Allyl Sorbitol (**Example 2**), 0.250 g of 12-hydroxy stearic acid, 0.250 g of lauryl sulfuric acid Na, and 60 g of methanol. The mixture was heated to reflux for one hour with stirring. The reaction was allowed to cool to room temperature. The methaol was rotor evaporated, then dried in a vacuum oven at 80°C for 2 hours, to give 9.62 g of product as a white solid. M.P. 203-204°C.

Example 21
Bis-1,3:2,4-(3',4' dimthylbenzylidene) 1-Methyl Sorbitol

2,3,4,6-Tetra-*O*-benzyl-D-glucono-1,5-lactone (21a)

27 g of 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (50 mmol) was dissolved in 153 mL of DMSO to form a clear solution. 102 mL of acetic anhydride was added dropwise. The resultant clear solution was allowed to stir at room temperature overnight. After 17 hours, GC-MS showed the lactone was gone and a new compound was observed. The yellow solution was poured into 600 mL of water and sat in a separation funnel overnight. The precipitated oil was passed through a silica gel column, eluted first with cyclohexane then gradually increasing polarity by adding acetone until the final eluent was cyclohexane: acetone = 2:1. The appropriate portions were

collected and evaporated to give a pale syrup. 25.2 g, yield: 94%. IR (v cm^{-1}) 2867, 1752.

3,4,5,7-Tetra-*O*-benzyl-1-deoxy-D-*gluco*-heptulopyranose (21b)

18 g (33 mmol) of **21a** was dissolved in 200 mL of anhydrous THF under nitrogen. Cooled to -78°C. 45 mL of MeLi (1.6 M, 72 mmol) was added by a syringe. After 1 hour at -78°C, the reaction was quenched by a solution of 7 g of NH_4Cl in 200 mL of H_2O. TLC showed no starting material left, while a new spot corresponding to the product appeared. The mixture was extracted by 3 X 150 mL of ethyl acetate, washed by brine, dried over Na_2SO_4. After evaporation, a thick pale yellow oil was obtained which was turned into a white solid (17.6 g, 95% yield) with a melting point of 92-93°C. 300 MHz ^1H NMR($CDCl_3$) δ: 1.41 (s, 3H, CH_3); 2.58 (s, 1H, OH); 3.35-3.38 (d, 1H); 3.65-3.72 (m, 3H); 3.93-3.99 (m, 2H); 4.50-4.95 (m, 8H, 4-CH_2), 7.14-7.36 (m, 20H). ^{13}C NMR ($CDCl_3$) δ: 26.59, 68.81, 71.55, 73.42, 74.85, 75.58, 75.68, 78.42, 83.18, 83.63, 97.36, 127.58, 127.65, 127.74, 127.82, 127.84, 127.91, 128.28, 128.32, 128.36, 128.41, 137.87, 138.21, 138.25, 138.64.

1,3,4,5-Tetrakis-benzyloxy-heptane-2,6-diol (21c+21c')

To a clear solution 5.54 g (10 mmol) of **21b** in 60 mL of THF, 0.5 g (12.5 mmol) of 95% $LiAlH_4$ was added. The mixture was allowed to stir under an ice-bath for 4 hours. TLC showed all starting material was gone with two very close new spots appearing. The reaction was carefully quenched with 2N HCl, then extracted with ethyl acetate. The combined organic phase was washed with aqueous $NaHCO_3$, then brine, and dried over sodium sulfate. A colorless syrup (5.5 g, 99% yield) was obtained after solvent was

evaporated. The ratio of 1.048-1.069 ppm (doublet, **21c**): 1.170-1.191 ppm (doublet, **21c'**) was 45%:55%, based on NMR.

Heptane-1,2,3,4,5,6-hexaol (21d+21d')

To a solution of 2.4 g (4.3 mmol) of **21c** in 100 mL of ethanol, 0.6g of 5% Pd-C was added. The mixture was hydrogenated at initial hydrogen pressure at 63 psi. After 6 hours, the catalyst was filtered off and washed with methanol-water. The combined solution was evaporated to give a white solid. 0.80 g, yield: 95%. 300 MHz ^{1}H NMR(D_2O) δ: 1.186-1.237 (two doublet, 3H), 3.537-3.988 (m, 7H).

Bis-1,3:2,4-(3',4' dimthylbenzylidene) 1-Methyl Sorbitol (21)

To a solution of 4.65 g (24 mmol) of **21d+21d'** in 100 mL of acetic acid was added 4.77 g (36 mmol) of 3,4-dimethyl benzaldehyde. The mixture was allowed to stir at room temperature overnight. The resultant gel was neutralized by KOH-H_2O. The white solid (4.2 g) was collected by filtration and suspended in boiling water. The suspension was filtered hot and the solid was washing with 7X100ml boiling water. The solid was then suspended in 50 mL of boiling methanol and filtered again. 2.30 g of dry, white solid was obtained with yield of 25%. GC-MS showed the purity was 98.3%. Melting point: 259-261°C. 300 MHz ^{1}H NMR(DMSO-d_6) δ: 1.23-1.25 (doublet, 3H), 2.21-2.23 (m, 12 H), 3.40-4.80 (m, 9H), 5.55-5.59 (doublet, 2H), 7.10-7.22 (m, 6H).

Example 22

Compositions containing various levels of the acetal of examples 2-21, coadditives (0.05 wt. % Irganox 1010, 0.1 wt. % Irgafos 168, and 0.08 wt. % calcium stearate) and the balance polypropylene homopolymer or

polypropene random copolymer (3% ethylene content) were dry blended in a mechanical mixer, extruded through a single screw extruder at 240°C and pelletized. Plaques were prepared (1.27 mm thick) by injection molding the pellets at 220°C.

The Tc and haze were measured, and the results are reported in Table 2. Millad 3988® is a registered trademark of Milliken and Company of Spartanburg, South Carolina. Millad 3988® is a commercially distributed clarifying agent product that employs bis(3,4-dimethylbenzylidene sorbitol)("DMDBS"), as shown and described in United States Patent No. 5,049,605.

TABLE 2: Percent Haze Measurements for Various Compounds

Polymer	Example	Concentration (ppm)	Tc (°C)	Haze(%)
RCP PP	(Control)	___	101.2	44.3
RCP PP	Millad 3988®	2500	113.6	7.2
RCP PP	2	6000	115.1	4.9
RCP PP	3	3500	109.4	8.8
RCP PP	4	5000	113.1	10.5
RCP PP	5	5000	107.8	17.2
RCP PP	6	2000	105.2	23.3
RCP PP	8	5000	109.0	8.9
RCP PP	10	5000	109.6	11.3
RCP PP	11	5000	111.9	21.8
RCP PP	12	5000	110.8	19.9
RCP PP	13	5000	109.5	8.4
RCP PP	14	5000	111.5	5.6
RCP PP	15	5000	105.8	8.8
RCP PP	16	3000	107.0	18.9
RCP PP	19a	5000	113.1	6.5
RCP PP	19b	5000	110.6	17.3
RCP PP	20	5000	114.6	5.7
RCP PP	21	2500	109.2	23.6
PP	(Control)	____	116.6	58.1
PP	Millad 3988®	2500	124.0	11.7
PP	2	5000	125.2	7.5

In some applications of the invention, the nucleating agent composition may be added to the polymer resin at a concentration of from about 0.005 to about 3 weight percent. In other applications, a concentration of between about 0.01 and about 1 weight percent may be employed. In other applications, a concentration of between about 0.025 and about 0.5 weight percent of the composition is useful.

Concentrates of up to 50 weight percent of the nucleating agent in resin may also be prepared for blending with additional resin prior to molding. Typically, concentrates containing 33 weight percent or less of the nucleating agent in resin are used commercially.

The resin may be extruded a second time immediately before being processed into a finished article by, for example, injection molding, extrusion blow molding, injection blow molding, stretch blow molding, compression molding, rotational molding, profile extrusion, sheet extrusion, thermal forming, film extrusion, and film extrusion with orientation.

Gel Formation and Testing

Solid gels also were produced comprising the inventive substituted-alditol derivatives through recognized, simple methods. In particular, specific organic solvents were combined with the additives in certain concentrations and mixed thoroughly. The resultant mixture was then heated to a temperature between about 170°F (77°C) and 300°F (149°C), as indicated below, under agitation for between 5 and 120 minutes. The resultant solution

was then poured into a mold to produce a gel stick. The solvents listed are not intended to be exhaustive as to the potential types which may be utilized to form gels with the inventive substituted-alditol derivatives, and thus are merely listed as preferred solvents for such purposes. The examples below were analyzed empirically and by touch to determine if a gel actually formed and the hardness properties as well as any formed gels. Results are reported in **Table 3**.

Table 3: Gel Sample Data

Sample Number	SOLVENT	ADDITIVE (Example # above)	DBS Conc. (Weight %)	Gel Formation (Y/N)	Gel Character (Hard/Soft)
1	1,2-Propanediol	2	1	Y	Hard
2	1,3-Propanediol	2	1	Y	Hard
3	2-Chlorotoluene	2	1	Y	Soft
4	Toluene	2	1	Y	Soft
5	Benzonitrile	2	1	Y	Soft
6	1,2-Propanediol	13	1	Y	Hard
7	2-Chlorotoluene	13	1	Y	Hard
8	Benzonitrile	2	3	Y	Hard
9	1,2-Propanediol	2	3	Y	Hard
10	1,3-Propanediol	2	3	Y	Hard
11	2-Chlorotoluene	2	3	Y	Soft
12	1,2-Propanediol	13	3	Y	Hard
13	2-Chlorotoluene	13	3	Y	Hard
14	1,2-Propanediol	18	1	Y	Hard
15	1,3-Propanediol	18	1	Y	Hard

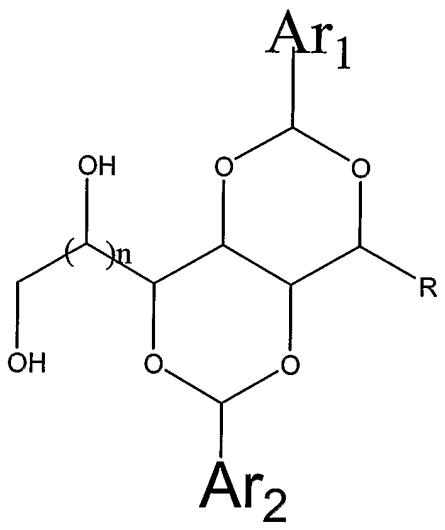
Thus, the inventive substituted-alditol derivatives provide excellent gelling capabilities for solvents, depending upon their concentration without the target solvents.

It is understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not

intended as limiting the broader aspects of the present invention, which broader aspects are embodied in the exemplary constructions. The invention is shown by example in the appended claims.

CLAIMS:

1. A method of nucleating a polyolefin composition, the method comprising in part combining with said polyolefin composition a compound, said compound having the structure:



wherein:

n is 0, 1 or 2;

Ar_1 and Ar_2 are independently selected from substituted or unsubstituted aryl-containing groups; and

R is selected from the group consisting of: alkenyls, alkyls, alkoxy, hydroxyl alkyls, alkyl-halides and derivatives thereof.

2. The method of claim 1 wherein n = 0.

3. The method of claim 1 wherein n = 1.

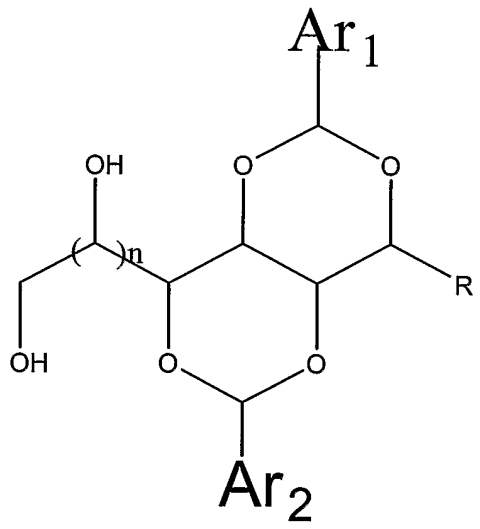
4. The method of claim 1 wherein n = 2.

5. The method of claim 2 wherein R comprises an allyl.

6. A polymer containing the compound of claim 1.

7. An article of manufacture made from the polymer of claim 6.

8. A method of nucleating a polyolefin composition, the method comprising combining with said polyolefin composition a compound, said compound having the structure:



wherein:

n is 0, 1 or 2;

Ar_1 and Ar_2 are independently selected from substituted or unsubstituted aryl-containing groups; and

wherein R is selected from the group consisting of:

$-CH_3$; $-CH_2CH_3$;

-CH2CH2CH3; $-CH_2CH_2CH_2CH_3$;

$-CH_2CH=CH_2$; $-CH(CH_3)CH=CH_2$;

$CH_2CH\text{-}X\text{-}CH_2\text{-}X'$; $CH_2CH_2\text{-}X''\text{-}CH_2\text{-}CH_3$;

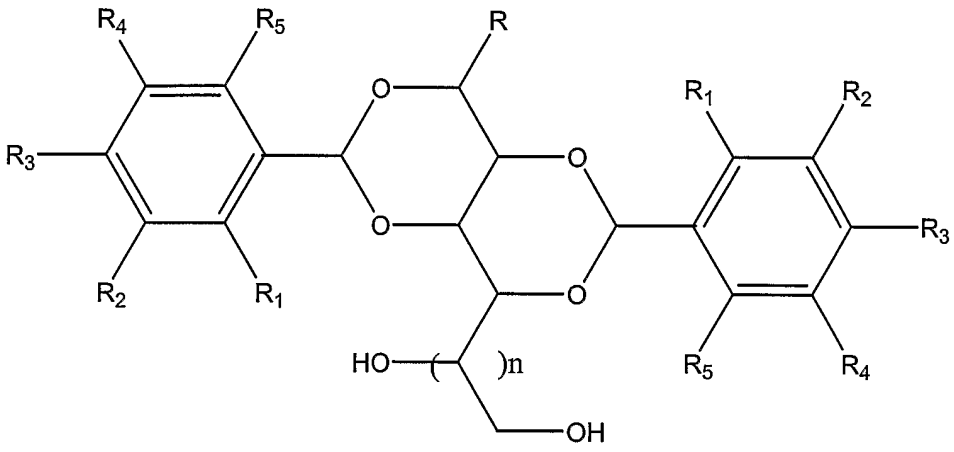
$CH_2CH\text{-}X'''\text{-}CH_2OH$; $-CH\text{-}OH\text{-}CH\text{-}OH\text{-}CH_2\text{-}OH$; and

wherein X, X', X'' , and X''' comprise independently selected halide groups.

9. The method of claim 8, further wherein Ar_1 and Ar_2 are independently selected from the group of substituted benzaldehydes including: benzaldehyde, 4-ethylbenzaldehyde, 4-isobutylbenzaldehyde, 4-fluoro-3-methylbenzaldehyde, 5,6,7,8-tetrahydro-2-naphthaldehyde, 3-methylbenzaldehyde, 4-propylbenzaldehyde, 4-butylbenzaldehyde, 4-methoxybenzaldehyde, 3-chlorobenzaldehyde, 3,4-dimethylbenzaldehyde, 3,5-difluorobenzaldehyde, 3-fluorobenzaldehyde, 4-fluorobenzaldehyde, 3-bromo-4-fluorobenzaldehyde, 3-methyl-4-methoxybenzaldehyde, 2,4,5-trimethylbenzaldehyde, 4-chloro-3-fluorobenzaldehyde, 4-methylbenzaldehyde, 3-bromobenzaldehyde, 4-methoxybenzaldehyde, 3,4-dichlorobenzaldehyde, 4-fluoro-3,5-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 4-bromobenzaldehyde, 3-ethoxybenzaldehyde, 4-allyloxybenzaldehyde, 3,5-dimethylbenzaldehyde, 4-chlorobenzaldehyde, 3-methoxybenzaldehyde, 4-(trifluoromethyl)benzaldehyde, 2-naphthaldehyde, 4-isopropylbenzaldehyde, 3,4-diethoxybenzaldehyde, 3-bromo-4-ethoxybenzaldehyde, piperonal, 3,4-dimethoxybenzaldehyde, 4-carboxybenzaldehyde, 3-hex-1-ynylbenzaldehyde, and 2-chlorobenzaldehyde. Preferred di-acetals of the present invention include 1,3:2,4-bis(4-ethylbenzylidene)-1-allyl-sorbitol, 1,3,2,4-bis(3'-methyl-4'-

fluoro-benzylidene)-1-propyl-sorbitol, 1,3,2,4-bis(5',6',7',8'-tetrahydro-2-naphthaldehydebenzylidene)-1-allyl-xylitol, bis-1,3,2-4-(3',4'-dimethylbenzylidene)-1"-methyl-2"-propyl-sorbitol, and 1,3,2,4-bis(3',4'-dimethylbenzylidene)-1-propyl-xylitol.

10. A method of nucleating a polyolefin composition, the method comprising in part combining with said polyolefin a compound, said compound having the structure:



wherein n is 0, 1, or 2;

R is a non-hydrogen group;

R_1, R_2, R_3, R_4, and R_5 each are independently selected from the group consisting of hydrogen, alkyls, alkynyls, alkoxy, carboxy, halogens, and phenyls.

11. The method of claim 10 wherein the non-hydrogen group R is selected from:

$-CH_3$; $-CH_2CH_3$;

-CH2CH2CH3; $-CH_2CH_2CH_2CH_3$;

$-CH_2CH=CH_2$; $-CH(CH_3)CH=CH_2$;

$-CH_2CH\text{-}X\text{-}CH_2\text{-}X'$; $CH_2CH.X''\text{-}CH_2\text{-}CH_3$;

$-CH_2CH\text{-}X'''\text{-}CH_2OH$; and -CH-OH-CH-OH-$CH_2$-OH;

wherein X, X', X" , and X"' comprise independently selected halogen groups.

12. The method of claim 11 wherein R comprises

--$CH_2CH=CH_2$.

13. The method of claim 11 wherein n = 0.

14. The method of claim 11 wherein n = 1.

15. The method of claim 11 wherein said polyolefin composition comprises polypropylene.

16. The method of claim 11 wherein R comprises

$-CH_2CH_2CH_3$.

17. The method of claim 16 wherein n = 0.

18. The method of claim 16 wherein n = 1.

19. The method of claim 11 wherein R comprises

-$CH(CH_3)CH=CH_2$.

20. The method of claim 19 wherein n = 1.

21. The method of claim 11 wherein R comprises

-$CH_2CHBrCH_2Br$.

22. The method of claim 21 wherein n = 1.

23. The method of claim 11 wherein R comprises.

-$CH_2CHBrCH_2OH$.

24. The method of claim 23 wherein n = 1.

25. The method of claim 16 wherein

R_1, R_2, R_4, and R_5 comprise hydrogen; and

R_3 comprises an alkyl.

26. The method of claim 25 wherein said alkyl comprises -C_2H_5.

27. The method of claim 16 wherein:

R_1 comprises hydrogen;

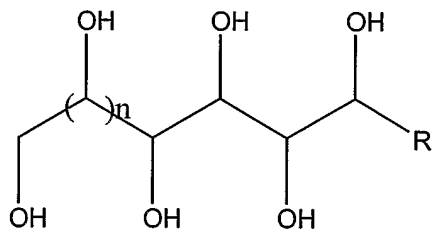
R_2 comprises -CH_3;

R_3 comprises -F;

R_4, and R_5 each comprise hydrogen.

28. A method of nucleating a polyolefin plastic composition, said composition comprising at least one polymer selected from aliphatic polyolefins and copolymers made from at least one aliphatic olefin and one or more ethylenically unsaturated comonomers, said method further comprising applying to said polyolefin plastic composition a compound formed by providing:

(a) at least one mono-, di-, or tri-acetal of a substituted alditol compound:

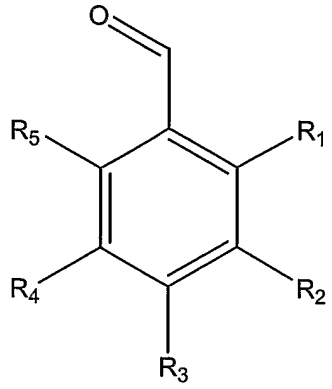


wherein:

n is 0, 1 or 2;

R is independently selected from alkenyl, alkyl, alkoxy, hydroxy alkyls, and alkyl-halides; and

(b) in combination with said substituted alditol at least one mole of substituted or unsubstituted benzaldehyde per mole of substituted alditol, said benzaldehyde being provided as shown:



wherein:

R_1, R_2, R_3, R_4, and R_5 each are independently selected from the group consisting of hydrogen, alkyls, fluorocarbons, alkenyls, alkynyls, alkoxy, carboxy, halogens, cyclic groups, and phenyls.

29. The method of claim 28 wherein said benzaldehyde(s) are independently selected from the group of benzaldehyde(s) including: benzaldehyde, 4-ethylbenzaldehyde, 4-isobutylbenzaldehyde, 4-fluoro-3-methylbenzaldehyde, 5,6,7,8-tetrahydro-2-naphthaldehyde, 3-methylbenzaldehyde, 4-propylbenzaldehyde, 4-butylbenzaldehyde, 4-methoxybenzaldehyde, 3-chlorobenzaldehyde, 3,4-dimethylbenzaldehyde, 3,5-difluorobenzaldehyde, 3-fluorobenzaldehyde, 4-fluorobenzaldehyde, 3-bromo-4-fluorobenzaldehyde, 3-methyl-4-methoxybenzaldehyde, 2,4,5-trimethylbenzaldehyde, 4-chloro-3-fluorobenzaldehyde, 4-methylbenzaldehyde, 3-bromobenzaldehyde, 4-methoxybenzaldehyde, 3,4-dichlorobenzaldehyde, 4-fluoro-3,5-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 4-bromobenzaldehyde, 3-ethoxybenzaldehyde, 4-allyloxybenzaldehyde, 3,5-dimethylbenzaldehyde, 4-chlorobenzaldehyde, 3-methoxybenzaldehyde, 4-(trifluoromethyl)benzaldehyde, 2-naphthaldehyde,

4-isopropylbenzaldehyde, 3,4-diethoxybenzaldehyde, 3-bromo-4-ethoxybenzaldehyde, piperonal, 3,4-dimethoxybenzaldehyde, 4-carboxybenzaldehyde, 3-hex-1-ynylbenzaldehyde, and 2-chlorobenzaldehyde. Preferred di-acetals of the present invention include 1,3:2,4-bis(4-ethylbenzylidene)-1-allyl-sorbitol, 1,3,2,4-bis(3'-methyl-4'-fluoro-benzylidene)-1-propyl-sorbitol, 1,3,2,4-bis(5',6',7',8'-tetrahydro-2-naphthaldehydebenzylidene)-1-allyl-xylitol, bis-1,3,2-4-(3',4'-dimethylbenzylidene)-1"-methyl-2"-propyl-sorbitol, and 1,3,2,4-bis(3',4'-dimethylbenzylidene)-1-propyl-xylitol.

30. The method of claim 28 wherein R is alkenyl.

31. The method of claim 30 wherein said alkenyl is an allyl group.

32. A method of preparing an acetal-based nucleating agent, said method comprising the steps of:

(a) reacting a polyhydric alcohol and an alkenyl group to form a first compound; and

(b) reacting in a condensation reaction said first compound with an aromatic aldehyde to form said acetal-based nucleating agent.

33. The method of claim 32 wherein said method further comprises a step of:

(c) combining with said acetal-based nucleating agent a co-additive.

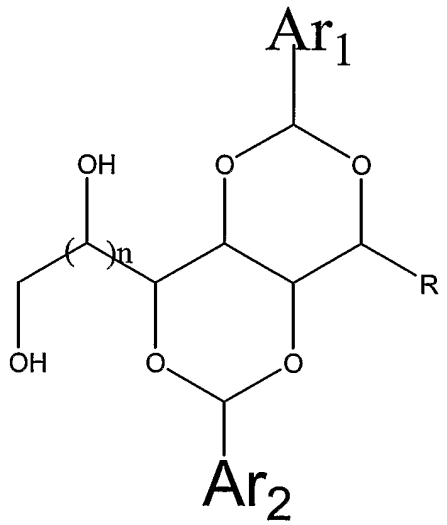
34. The method of claim 32 wherein said alkenyl group comprises an allyl.

35. A method of making a molded article, said article comprising in part a polyolefin, said article further comprising an acetal compound, said acetal compound being formed by the process of:

(a) reacting a polyhydric alcohol and an alkenyl group to form a first compound; and

(b) reacting in a condensation reaction said first compound with an aromatic aldehyde to form an acetal compound.

36. A method of making a formed polyolefin article comprising a nucleating compound, said article being made by combining or blending a polyolefin resin and a nucleating compound to form a blended polyolefin material, said nucleating compound comprising:



wherein:

n is 0, 1 or 2;

Ar_1 and Ar_2 are independently selected from substituted or unsubstituted aryl-containing groups; and

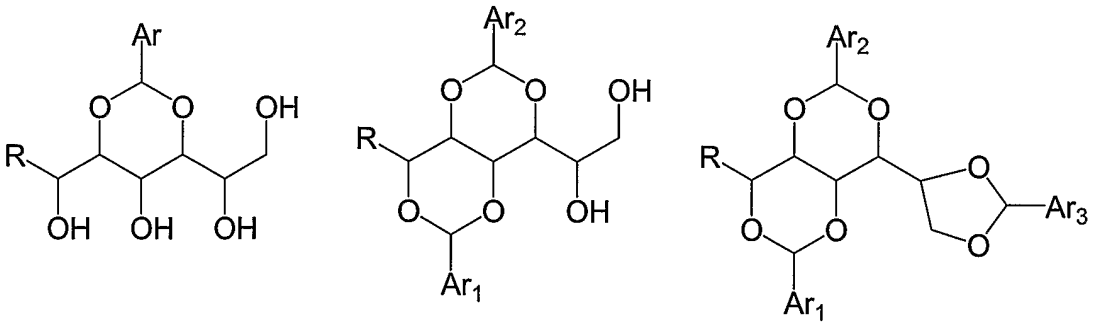
R is selected from the group consisting of: alkenyls, alkyls, alkoxy, hydroxyl alkyls, and alkyl-halides.

37. A polyolefin article containing the nucleating compound of claim 36.

38. The polyolefin article of claim 37 wherein said polyolefin article comprises polypropylene.

39. A polyolefin composition containing a nucleating agent, said nucleating agent being made by combining a polyolefin with a compound, said compound having a structure selected from the group of structures set forth in (I) below:

(I)



wherein:

Ar, Ar_1 and Ar_2 are independently selected from substituted or unsubstituted aryl-containing groups; and

R is selected from the group consisting of: alkenyls, alkyls, alkoxy, hydroxyl alkyls, alkyl-halides and derivatives thereof.

40. The composition of claim 39, wherein said method further comprises combining with said polyolefin composition a co-additive.

41. The composition of claim 40 wherein said co-additive comprises lauryl sulfuric acid Na.

42. The composition of claim 40 wherein said co-additive comprises an alkali salt of an amino acid.

43. The composition of claim 40 wherein said co-additive comprises an aliphatic alcohol.

44. The composition of claim 40 wherein said co-additive comprises an acid-containing compound.