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(54) Title: ASYMMETRIC BENZALDEHYDE ALDITOL DERIVATIVES, METHODS OF MAKING THEREOF, AND COMPOSITIONS AND ARTICLES CONTAINING SAME

(57) Abstract: Plastic additives which are useful as nucleating agents and which are especially useful for improving the optical properties of polymeric materials are provided. More particularly, this invention relates to certain asymmetric substituted dibenzylidene sorbitol acetals having various types of pendant groups on the benzyl systems thereof, such as, without limitation, opposing electron withdrawing and electron donating groups (to form dipolar compounds), mixed alkyl-halogen or other types groups, multi-alkyl substitutions, cyclic pendant groups, and the like. Polymer compositions comprising such compounds are also contemplated which may be utilized within, as merely examples, food or cosmetic containers and packaging. These inventive asymmetric dibenzylidene sorbitol acetals are also useful as gelling agents for water and organic solvents, particularly those used in the preparation of antiperspirant gel sticks.

ASYMMETRIC BENZALDEHYDE ALDITOL DERIVATIVES, METHODS OF MAKING THEREOF, AND COMPOSITIONS AND ARTICLES CONTAINING SAME

Field of the Invention

This invention relates to plastic additives which are useful as nucleating agents and which are especially useful for improving the optical properties of polymeric materials. More particularly, this invention relates to certain asymmetric substituted dibenzylidene sorbitol acetals having various types of pendant groups on the benzyl systems thereof, such as, without limitation, opposing electron withdrawing and electron donating groups (to form dipolar compounds), mixed alkyl-halogen or other types groups, multi-alkyl substitutions, cyclic pendant groups, and the like. Polymer compositions comprising such compounds are also contemplated which may be utilized within, as merely examples, food or cosmetic containers and packaging. These inventive asymmetric dibenzylidene sorbitol acetals are also useful as gelling agents for water and organic solvents, particularly those used in the preparation of antiperspirant gel sticks.

Background of the Prior Art

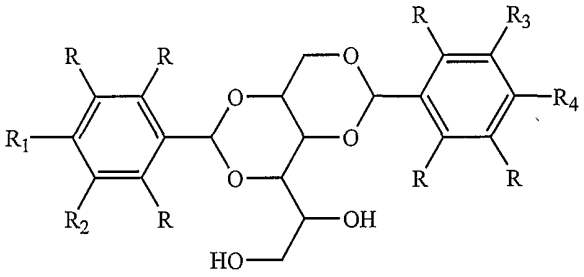
All U.S. Patents cited below are herein entirely incorporated by reference.

Numerous attempts have been made to improve the clarity and physical properties of polyolefins through the incorporation of certain kinds of additives. Certain applications require good clarity or transparency characteristics. These include certain types of plastic plates, sheets, films, containers, and syringes that need to exhibit clarity primarily to facilitate identification of articles, etc., stored, wrapped, and/or covered therewith. Such commercially available plastic additives fall into two categories termed "melt sensitive" and "melt insensitive". Melt sensitive additives possess melting points below or near the normal processing temperatures of polyolefin-based resins and include dibenzylidene sorbitol (DBS) systems. Melt insensitive additives do not melt at normal processing temperatures and include sodium benzoate and salts of organic phosphates as examples.

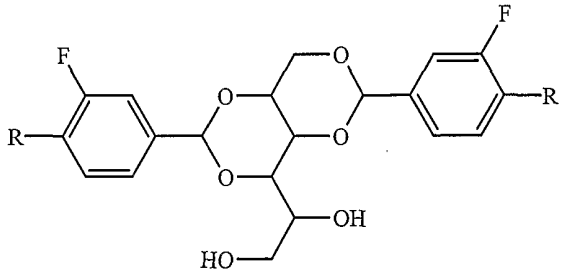
U.S. Pat. No 4,016,118 to Hamada, et al. teaches that a polyolefin plastic composition containing 0.1% to 0.7% dibenzylidene sorbitol (DBS) as an additive will show improved transparency and reduced molding shrinkage over compositions containing a substituted

benzoic acid salt. Additional advancements in sorbitol-based clarification technology have been driven by the need for improved transparency, reduction of plate-out during processing, and improved organoleptic properties (e.g., odor, taste, etc.). In order to overcome these deficiencies, many derivatives of DBS in which the aromatic rings are substituted with various groups have been proposed.

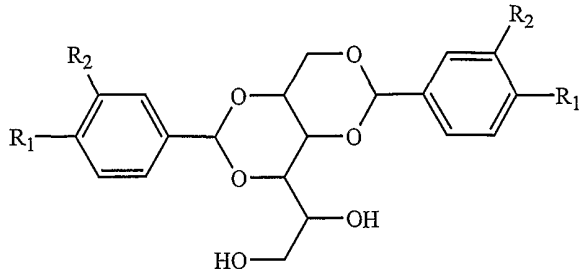
Mahaffey, in U.S. Pat. No. 4,371,645 discloses a series of dibenzylidene sorbitols having the general formula:



wherein R, R_1, R_2, R_3, and R_4, are selected from hydrogen, lower alkyl, hydroxy, methoxy, mono- and di-alkylamino, amino, nitro, and halogen, with the proviso that at least one of R_1, R_2, R_3, and R_4 is chlorine or bromine. Effective concentrations of the disclosed substituted DBS derivatives range from 0.01 to about 2 percent by weight of the total composition weight. Further improvements in transparency characteristics are disclosed by Titus, et al. in U.S. Pat. No. 4,808,650. In this patent mono and disubstituted DBS derivatives having the formula:



in which R may be hydrogen or fluorine provide improved clarity applications in polyolefins. Rekers, in U.S. Pat. No. 5,049,605 discloses a series of dibenzylidene sorbitols having the general formula:



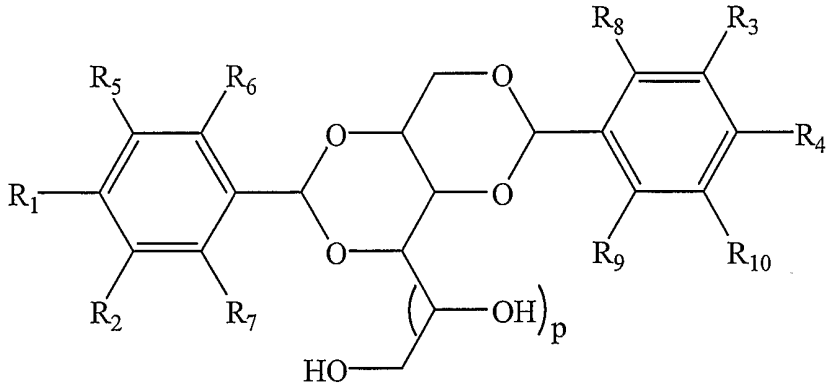
in which R_1 and R_2 are independently selected from lower alkyl groups containing 1-4 carbons which can also form a carbocyclic ring containing up to 5 carbon atoms. Also disclosed are polyolefin plastics containing the above group of dibenzylidene sorbitols. Videau, in U.S. Patent No. 5,696,186 discloses substituted DBS derivatives with an alkyl group (methyl, ethyl, or the like) or halogen (fluorine, chlorine, or the like) on the benzene rings for use as nucleation/clarification agents in polyolefins.

Dibenzylidene sorbitol (DBS) is a well known gelling agent for a variety solvent systems as disclosed in U.S. Pat. No. 4,154,816, Roehl et al.; U.S. Pat. No. 4,816,261, Luebbe et al.; and U.S. Pat. No. 4,743,444 to McCall. U.S. Pat. No. 5,609,855 to Oh et al. and PCT Patent Application WO/92/19221 to Juneja et al. disclose that di(meta-fluorobenzylidene) sorbitol and di(meta-chlorobenzylidene) sorbitol are extremely useful as gelling agents in the preparation of antiperspirant gel sticks. These two respective DBS systems form effective hard gels and show improved gel stability in the acidic environment of antiperspirant formulations.

Detailed Description of the Invention

According to the present invention, a polyolefin plastic composition having improved transparency is provided which comprises 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 di-acetal of an alditol (such as sorbitol, xylitol, and ribitol) conforming to at least one of the following structures (I), (II), (III), or (IV):

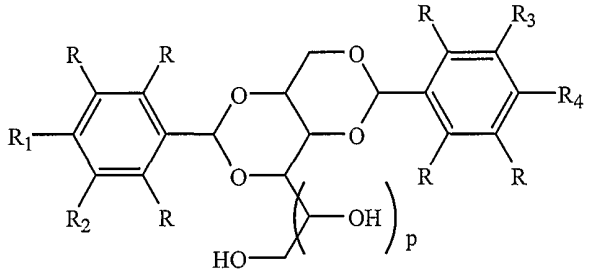
(I)



wherein p is 0 or 1, R_5, R_6, R_7, R_8, R_9, and R_{10} are each the same or different and are selected from electron donating groups, such as hydrogen, lower alkyl groups containing 1-4 carbon

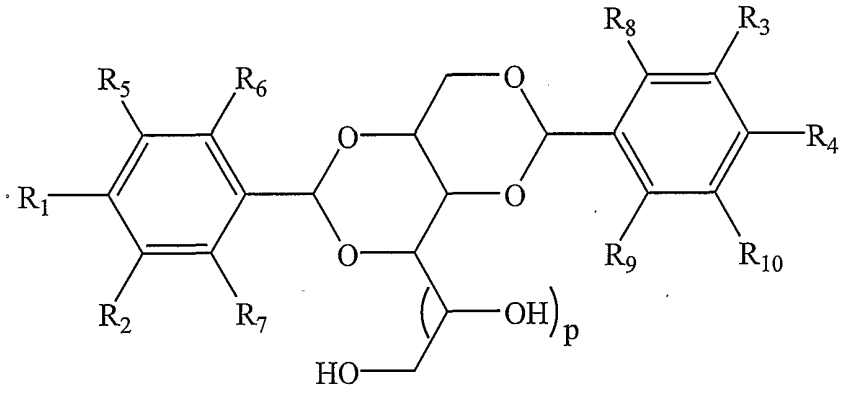
atoms, lower alkoxy groups, and electron withdrawing groups, such as halogens (meaning fluorine, chlorine, bromine, and iodine); R_1, R_2, R_3, and R_4 are the same or different and are selected from electron donating groups, such as hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, or any two are combined to form a carbocyclic or methylenedioxy ring, and electron withdrawing groups, such as nitro and halogens; with the first proviso that if one of said R_1, R_2, R_3, or R_4 groups is nitro, then no other nitro groups are present anywhere on the compound; with a second proviso that at least at least two electron withdrawing groups (other than the nitro group, above) must be present and must be present as either the pair of R_1 and R_2 or the pair of R_3 and R_4 such that if one pair comprises such electron withdrawing groups, the other pair must comprise electron donating groups and the same ring system comprising such electron donating groups must not comprise any electron withdrawing groups;

(II)



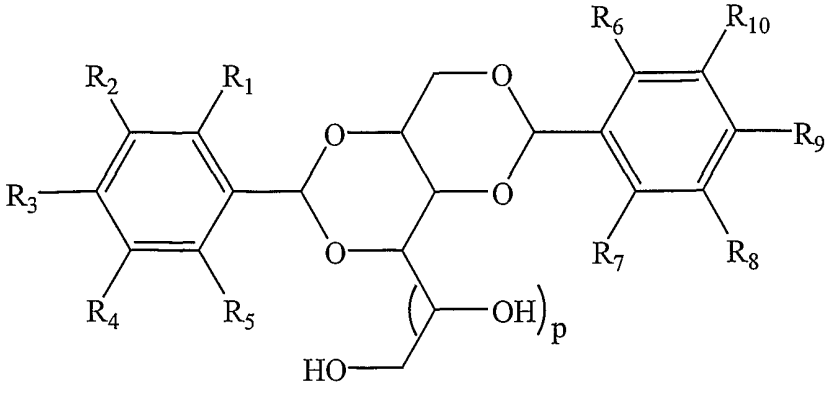
wherein R is selected from hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and fluorine; R_1, and R_2, are selected from lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and halogens; R_3, and R_4 are selected from lower alkyl groups containing 1-4 carbon atoms and which together may form a carbocyclic ring containing up to 6 carbon atoms, lower alkoxy groups, halogens, and hydrogen; with the proviso that only one of R_1 and R_2 is halogen; and p is 0 or 1;

(III)



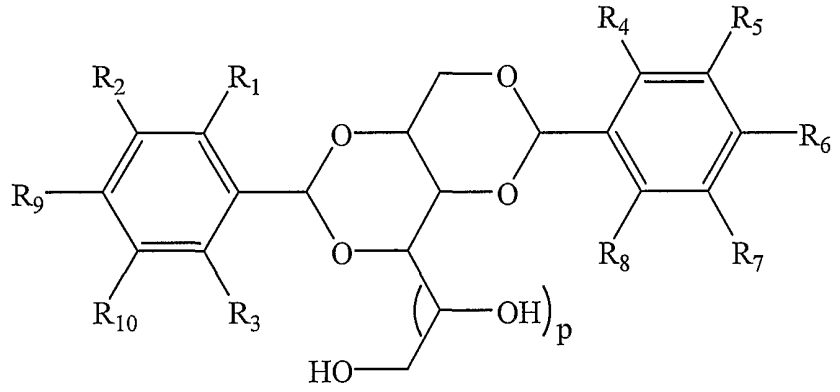
wherein p is 1 or 2, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are independently selected from the group consisting of hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, nitro, halogen, or any two adjacent groups may be combined to form a cyclic group; R_1, R_2, R_3, and R_4 are independently selected from the group consisting of hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, fluorine, and trifluoroalkyl groups containing 1-4 carbon atoms; with the proviso that either one of R_1 and R_2 or R_3 and R_4 is fluorine or trifluoroalkyl, as defined above, such that if one of said groups is a fluorine or trifluoroalkyl on a first ring system, then no other fluorines are present on the same first ring system, and, if said first ring system has only one fluorine pendant group in the 3- or 4-position, then the other ring system cannot have a single fluorine pendant group; and with a second proviso that if said first ring system comprises a fluorine in the 3- or 4-position, and an alkyl group in the 3- or 4-position, then the other ring system cannot exhibit the same pendant groups in the same positions as said first ring system;

(IV)



or

(V)



wherein for both (IV) and (V), p is 1 or 2, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are independently selected from the group consisting of hydrogen, alkyl groups containing 3-6 carbon atoms, alkoxy groups containing 1-6 carbon atoms, phenyl, naphthyl, and substituted benzyl, or any two adjacent groups may be combined to form a cyclic group, wherein said cyclic group is selected from methylenedioxy, cyclohexyl, and cyclopentyl; with the provisos that at least two groups of R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are a group other than hydrogen, that at least one pendant group other than hydrogen is present on each ring, and that the entire compound is asymmetric.

Preferably, though not necessarily, one and only one of the benzylidene substituents is 3,4-dimethyl substituted for these above-listed structures. The important characteristic of such compounds is that they are asymmetric and meet the basic definitions set forth above. The 3,4-disubstitution, however, has been found to provide the best overall performance within target polyolefins and gelling solvents.

For the structure of Formula (I), above, preferably, the electron donating group-containing ring (and electron withdrawing group-containing ring) must be 3,4-disubstituted with such groups, although such a limitation is not required. Such inventive compounds (and not just the polyolefin compositions comprising such compounds) are also encompassed individually and in combination within the scope of this invention, particularly in its broadest sense an asymmetric alditol di-acetal comprising at least two arylidene components wherein one of said arylidene components possesses either a single nitro pendant group or at least two electron drawing pendant groups and the other arylidene component must comprise at least

two electron donating pendant groups. Such compounds are novel in structure and in utilization as thermoplastic additives.

The individual compounds as defined for Structure (II) are inventive compounds alone as well, broadly stated as asymmetric alditol di-acetal compounds comprising at least two arylidene components wherein one of said benzylidene components at least possesses one halogen pendant group in either the 3- or 4-position and one pendant group selected from lower alkyl and lower alkoxy in the 3- or 4- position.

Throughout this specification, the term "asymmetrical" as it pertains to di-acetals of alditols is intended to mean wherein such alditol acetals possess 1,3- and 2,4- acetal linkages derived from different aldehydes.

It should be appreciated with regard to the structural formula set forth above that while only the 1,3:2,4 isomer is represented, this structure is provided for convenience 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 so long as the compound contains two benzylidene acetal substitutents on the alditol moiety.

However, as noted above, the compounds conforming with the structures of most of the formulae above, may also be utilized individually within the target polyolefin formulations or combined in some manner and in any proportions as well. More particularly, it is contemplated that reaction product mixtures of isomeric compounds confirming to the structure of the formulae listed above as well as other most likely symmetrical dibenzylidene alditol compounds will be formed during production of the desired asymmetric compounds of this invention. It is important to note that the reaction necessary to produce the desired asymmetric diacetals requires the utilization of different benzaldehyde reactants. In such a reaction, invariably different diacetal compounds will be produced. For example, Example 1, below, below shows the production of a mixture of 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol, 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol, and 1,3:2,4-bis(3,4-dichlorobenzylidene) sorbitol simultaneously. Furthermore, Example 9, below, shows the production of a mixture of 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol, 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol, and 1,3:2,4-bis(4-fluoro-3-methylbenzylidene) sorbitol simultaneously. Due to the similar solubilities of such

DBS compounds (in each instance, not just in Examples 1 and 9), it has been found to be extremely difficult to separate these individual compounds from the reaction product mixture. Such a mixture thus not only includes the desired inventive asymmetric compound or compounds, but such a mixture is an inventive composition as well. Hence, the terms "diacetal compositions", as well as "reaction product mixtures" (as well as their singular forms) are intended to encompass such an inventive mixture including the desired asymmetrics.

In order to produce such diacetal compositions (and thus the inventive asymmetric compounds themselves), the starting materials must include the desired alditol (such as D-sorbitol), and at least two different substituted benzaldehydes (or one could be unsubstituted), including arylaldehydes. Generally, as noted above, the molar ratio of alditol to benzaldehyde reactant is at least 1:2 for diacetal formation. In this specific situation of producing asymmetric compounds, the same general molar ratio is followed (with the ability to use more or less of either type of reactant if desired); however, the benzaldehyde component is measured as a total amount of the at least two different benzaldehyde reactant compounds necessary for asymmetric production. Thus, the benzaldehyde component is split into at least two different measurements of the individual reactants utilized. Such a split of amounts can be as disparate as a range of from 1:25 to 25:1 of molar ratios of benzaldehydes, if desired. More likely, and more desired, however, is a range of from 1:5 to 5:1, preferably from 1:4 to 4:1, more preferably from 1:3 to 3:1, still more preferably from 1:2 to 2:1, and most preferably a molar ratio of substantially 1:1.

With such a required reaction of different benzaldehydes and alditol, one of ordinary skill in the art would theoretically expect that approximately 25% yield of each possible compound is realized. However, it appears that the asymmetrics unexpectedly are produced in greater yields (in combination upwards of from about 60 to 80%), well above the expected yield. Such a "reaction product" mixture has been found, unexpectedly, to be useful in providing excellent clarifying, nucleating, etc., properties within the target polyolefin. On the other hand, "physical" mixtures of individual inventive compounds (with other inventive compounds or with other types of DBS clarifiers) may also be followed to produce highly desirable clarity, nucleation, and the like, within target polyolefins. Thus, selected mixtures of from about 25 to 90% of (a) and from about 25 to 90% of another compound [or the same with (b)] are highly effective as well.

The preferred diacetals of the present invention are thus generally considered condensation products of sorbitol and at least two substituted benzaldehydes (or arylaldehydes). Examples of suitable substituted reactants include 3,4-dichlorobenzaldehyde, 3,4-dimethylbenzaldehyde, 3,4-difluorobenzaldehyde, 3,4-diethylbenzaldehyde, 2,4-dichlorobenzaldehyde, 2,4-difluorobenzaldehyde, 2,4-dimethylbenzaldehyde, 3,4-diethylbenzaldehyde, 3-nitrobenzaldehyde, 4-nitrobenzaldehyde, 3,4-dimethoxybenzaldehyde, 2,4-dimethoxybenzaldehyde, 3,4-diethoxybenzaldehyde, 2,4-diethoxybenzaldehyde, 6-formyltetralin, 5-formylindan, 3,4-methylenedioxybenzaldehyde (piperonal), 4-fluoro-3-methylbenzaldehyde, 3-fluoro-4-methylbenzaldehyde, 4-fluoro-2,3-dimethylbenzaldehyde, 3-fluoro-2,4-dimethylbenzaldehyde, 2,4-difluoro-3-methylbenzaldehyde, 4-fluoro-3,5-dimethylbenzaldehyde, 3-fluoro-4-methoxy-benzaldehyde, 4-chloro-3-methylbenzaldehyde, 3-chloro-4-methylbenzaldehyde, 4-chloro-2,3-dimethylbenzaldehyde, 3-chloro-2,4-dimethylbenzaldehyde, 3-chloro-4-methoxybenzaldehyde, 3-chloro-4-methoxy-2-methylbenzaldehyde, 3,4-dimethylbenzaldehyde, 4-methylbenzaldehyde, 2,4-dimethylbenzaldehyde, 2,4,5-trimethylbenzaldehyde, 2,4-diethylbenzaldehyde, 4-nitrobenzaldehyde, 2,4-dichloro-3-methylbenzaldehyde, 4-chloro-3,5-dimethylbenzaldehyde, 2,4-diisopropylbenzaldehyde, 2,4-di-*t*-butylbenzaldehyde, 2,4-dimethoxybenzaldehyde, 2,4,5-trimethoxybenzaldehyde, 2,4-diethoxybenzaldehyde, 4-n-pentylbenzaldehyde, 3-methyl-4-methoxybenzaldehyde, 4-methoxy-2,3-dimethylbenzaldehyde, 3-methoxy-2,4-dimethylbenzaldehyde, 2,4-dimethoxy-3-methylbenzaldehyde, 4-ethoxy-3,5-dimethylbenzaldehyde, and 3-isopropyl-4-methoxybenzaldehyde, and the like. Further examples of other aldehydes to be used in conjunction (and thus as the opposing benzylidene group on the target diacetal) with these possible subsituted benzaldehydes include, again, without limitation, benzaldehyde, 4-methyl benzaldehyde, 4-ethylbenzaldehyde, 4-propylbenzaldehyde, 4-butylbenzaldehyde, 4-fluorobenzaldehyde, 4-chloro-benzaldehyde, 4-bromobenzaldehyde, 3-fluorobenzaldehyde, 3-trifluoromethylbenzaldehyde, 3,4-dimethylbenzaldehyde, 3,5-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde, 2,3-dimethylbenz-aldehyde, 2,5-dimethylbenzaldehyde, 3,4-difluorobenzaldehyde, 3,4-dichloro-benzaldehyde, 3,4-dibromobenzaldehyde, 2,3,4-trimethylbenzaldehyde, 2,4,6-trimethylbenzaldhyde, 3,4,5-trimethylbenzaldehyde, 5,6,7,8-tetrahydro-2-naphthaldehyde, 3,4-dioxymethylene benzaldehyde, 5-formylindan, 6-formyltetralin, and other benzaldehydes, such as the above-listed halogen-alkyl substituted types.

Non-limiting preferred diacetals of the present invention thus include 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol, 1,3-O-(3,4-difluorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, , 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-difluorobenzylidene) sorbitol, 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethoxybenzylidene) sorbitol, , 1,3-O-(3,4-dimethoxybenzylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol, 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(5-indanylidene) sorbitol, , 1,3-O-(5-indanylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol, 1,3-O-(4-nitrobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-nitrobenzylidene) sorbitol, 1,3-O-(4-nitrobenzylidene):2,4-O-(3,4-methylenedioxybenzylidene) sorbitol, 1,3-O-(3,4-methylenedioxybenzylidene):2,4-O-(4-nitrobenzylidene) sorbitol, 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) xylitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dichlorobenzylidene) xylitol, 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol, 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(3-fluoro-4-methylbenzylidene) sorbitol, 1,3-O-(3-fluoro-4-methylbenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol, 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(4-chlorobenzylidene) sorbitol, 1,3-O-(4-chlorobenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol, 1,3-O-(4-chloro-3-methylbenzylidene):2,4-O-(3-chloro-4-methylbenzylidene) sorbitol, 1,3-O-(3-chloro-4-methylbenzylidene):2,4-O-(4-chloro-3-methylbenzylidene) sorbitol, 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(5',6',7',8'-tetrahydro-2-napthylidene) sorbitol, 1,3-O-(5',6',7',8'-tetrahydronapthylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol, 1,3-O-(4-Chloro-3-methylbenzylidene)-2,4-O-(5',6',7',8'-tetrahydro-2-napthylidene) sorbitol, 1,3-O-(5',6',7',8'-tetrahydronapthylidene):2,4-O-(4-chloro-3-methylbenzylidene) sorbitol, 1,3-O-(3-bromo-4-ethylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3-bromo-4-isopropylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3-bromo-4-methylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(4-chlorobenzylidene):2,4-O-(3-bromo-4-isopropylbenzylidene) sorbitol, 1,3-O-(4-fluorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-fluorobenzylidene) sorbitol, 1,3-O-(3-fluorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3-

fluorobenzylidene) sorbitol, 1,3-O-(3,4-diemthylbenzylidene):2,4-O-(4-trifluoromethylbenzylidene) sorbitol, 1,3-O-(4-trifluoromethylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, include 1,3-O-(4-t-butylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(t-butylbenzylidene) sorbitol, 1,3-O-(3,4-dimethoxybenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dimethoxybenzylidene) sorbitol, 1,3-O-(3,4-methylenedioxybenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-methylenedioxybenzylidene) sorbitol, 1,3-O-(4-isopropylbenzylidene):-2,4-O-(3,4-dimethylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-isopropylbenzylidene) sorbitol, 1,3-O-(3,4-dimethylbeznylidene):2,4-O-(2-naphthylbenzylidene) sorbitol, and 1,3-O-(2-naphthylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol. As noted below, these compounds may be produced as individual components within mixtures of different compounds formed through the reaction of the at least two different benzaldehydes (such as those listed above) and alditols (such as sorbitol).

The compositions of the present invention also include solvent gels containing 0.2% to 10% of the above diacetals as a gelling agent. Solvents useful herein include, as merely examples, lower monohydric alcohols, polyhydric alcohols, and mixtures thereof. Water may also be included as a portion of the solvent. However, the solvent will generally comprise water at levels no greater than 5% by weight of the final composition. Examples of solvents which may be utilized in the present invention include liquid polyethylene glycols (e.g., diethylene glycol, triethylene glycol), liquid polypropylene glycols (e.g., dipropylene glycol, tripropylene glycol), liquid polypropylene polyethylene glycol copolymers, ethanol, n-propanol, n-butanol, t-butanol, 2-methoxyethanol, 2-ethoxyethanol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, 1,2-butylene glycol, isopropanol, isobutanol, diethylene glycol monomethyl ether, diethylene glycol monoethylether, 1,3-butylene glycol, 2,3-butylene glycol, 2,4-dihydroxy-2-methylpentane, trimethylene glycol, glycerine, 1,3-butanediol, 1,4-butanediol, and the like, and mixtures thereof. As used herein, polyethylene glycols, polypropylene glycols, and polypropylene polyethylene glycol copolymers include alkyl ether derivatives of these compounds (e.g., ethyl, propyl, and butyl ether derivatives). Examples of such compounds are butyl ether derivatives of polypropylene polyethylene glycol copolymers, such as PPG-5-buteth-7.

These solvents are fully described, for example, in U.S. Pat. No. 4,518,582 to Schamper et al. and European Published Application 107,330 to Luebbe et al. incorporated herein by reference. The preferred solvents for use herein include liquid polyethylene glycols, liquid polypropylene glycols, liquid polypropylene polyethylene glycol copolymers, propylene glycol, 1,3-butylene glycol, and 2,4-dihydroxy-2-methylpentane (sometimes referred to as hexylene glycol), and mixtures thereof. Particularly preferred solvents include propylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, hexylene glycol, and mixtures thereof.

Other organic solvents useful herein include aromatics, halogenated aromatics, nitrated aromatics, ketones, amines, nitriles, esters, aldehydes, and mixtures thereof. Examples of solvents which may be utilized in the present invention include xylenes (o-, m-, and p-substituted), 2-chlorotoluene, fluorobenzene, nitrobenzene, benzonitrile, dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF), and 1-methyl-2-pyrrolidinone (NMP).

The diacetals of the present invention may be prepared by the reaction of one mole of sorbitol with about 1 mole each of two different benzaldehydes in the presence of an acid catalyst. The temperature employed in the reaction will vary widely depending upon the characteristics, such as melting points or boiling points, of the benzaldehydes employed as a starting material in the reaction. The reaction medium may be an aqueous medium or a non-aqueous medium. One very advantageous method that can be employed to prepare diacetals of the invention is similar to that described in U.S. Pat. No. 3,721,682, to Murai et al. (New Japan Chemical Company Limited), the disclosure of which is hereby incorporated herein by reference. While the disclosure of the patent is limited to dibenzylidene sorbitols, it has been found that the diacetals of the present invention may also be conveniently prepared by the method described therein. Additional methods for preparing DBS systems can be found in U.S. Pat. No. 5,731,474 to Scrivens et al., U.S. Pat. No. 4,902,807 to Kobayashi et al. which discloses DBS having an alkyl group or halogen for use as clarifying agents, and U.S. Pat. No. 5,106,999 to Gardlik et al. which discloses the preparation of di(meta-fluorobenzylidene) sorbitol, di(meta-chlorobenzylidene) sorbitol, and di(meta-bromobenzylidene) sorbitol.

Although such general methods can be followed, it has been unexpectedly and surprisingly found that the inventive combination of two different aldehydes (with different pendant groups attached thereto) to form a compound that conforms generally to the structure of Formula (I), above, as one example, thus especially with one benzaldehyde possessing electron donating groups in the 3,4- position and the other possessing electron withdrawing

groups in the 3,4- position (except 3- and 4-nitrobenzaldehyde), as described above, react in such a manner as to produce a non-statistical yield of a majority of asymmetric diacetal compounds. Theoretically, a total yield relatively close to a 25% individual yield of the four possible products from such a reaction is expected [thus 25% of the symmetrical 3,4-dimethyldibenzylidene sorbitol, 25% of the symmetrical 3,4-dichlorodibenzylidene sorbitol, and 25% each of the asymmetric products of 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol]. However, as noted in the specific example above, the resultant product mixture has an appreciable majority (about 63% by weight) of the dipolar asymmetric diacetals. The remaining products are present, but in much lower proportions as compared to their theoretical yields. Although such a result is not readily understood, without intending to be limited to any specific scientific theory, it is believed that such a phenomenon results due to the stability accorded the above-noted asymmetric compounds.

Furthermore, it has been determined that such Formula (I) dipolar asymmetric compounds provide excellent clarifying properties to polyolefin compositions (such as, preferably polypropylene). In fact, the haze characteristics of polypropylene articles clarified therewith have measured at levels below about 6%. Again, without intending to be limited to any specific scientific theory, it is believed that such excellent clarity results are provided by the substantially uniform orientation of these asymmetric diacetals within the target polypropylene itself. The other compounds of Formulae (II)-(V), above, also exhibit certain haze, nucleating, or other type of acceptable characteristics within thermoplastics as well.

Continuing with the phenomena available with the structures of Formula (I), above, it appears that, upon an initial production of a molten composition of polyolefin and clarifying agent, during the subsequent cooling to produce a solid article the clarifying agents form a fibrous network at high temperatures, on which the polypropylene recrystallizes at lower temperatures. The more uniform orientation of such a fibrous network, seemingly the more uniform orientation of crystallized polymer within the final solid article. With one end of the clarifying compound exhibiting a strong ability to withdraw electrons, and the other much weaker in such a respect or, more importantly, exhibiting a capacity to donate electrons, it has been theorized that the stronger withdrawing end will most likely attract (or be attracted to) the end of compound exhibiting electron donating abilities. Thus, within the molten polymer, it is believed that such an arrangement occurs readily, thereby providing a substantially uniform arrangement within the necessary fibrous network for recrystallization of the target

polymer. In such an instance, although some non-asymmetric compounds are present, it has been found that purification of the desired uniform asymmetric compound is highly desired, although it is not required to provide a clarifying agent that ultimately provides a desirable low haze characteristics within the final solid polyolefin article. Of course, preferably a pure formulation of asymmetric alone (and only one type of asymmetric, as two will be produced) is highly desired, although rather difficult to produce due to problems associated with the requisite separation procedures from the other three reaction products. Again, the other inventive compounds provide certain similar benefits as well.

The inventive sorbitol diacetals prepared by the above techniques may contain a minor or even a major portion of by-product monoacetal and triacetal as impurities (in addition to the aforementioned expected reaction product mixture of diacetals). Although it may not always be necessary to remove these impurities prior to incorporation of the diacetal into the polyolefin, it may be desirable to do so and such purification may serve to enhance the transparency of the resin produced thereby. Purification of the diacetal may be accomplished, for instance, by removal of the triacetal impurities by the extraction thereof with a relatively non-polar solvent. By removal of the impurities, the product may be purified so that the amount of diacetal in the additive composition contains, preferably, though not necessarily, at least about 90 percent and even up to 95 percent of the diacetal composition or more.

The proportion of diacetal in the composition of this invention is an amount sufficient to improve the transparency of the composition, generally from about 0.01 to about 2 percent by weight, preferably about 0.1 to about 1 percent by weight, based upon the total weight of the composition may be provided. When the content of the diacetal composition is less than about 0.01 percent by weight, the resulting composition may not be sufficiently improved in respect to transparency characteristics. When the content of diacetal composition is increased beyond about 2 percent by weight, no additional advantage can be observed.

The polyolefin polymers of the present invention may include aliphatic polyolefins and copolymers made from at least one aliphatic olefin and one or more ethylenically unsaturated comonomers. Generally, the comonomers, if present, constitute a minor amount, e.g., about 10 percent or less or even about 5 percent or less, of the entire polyolefin, based upon the total weight of the polyolefin. Such comonomers may serve to assist in clarity improvement of the polyolefin, or they may function to improve other properties of the polymer. Examples include acrylic acid and vinyl acetate, etc. Examples of olefin polymers whose transparency

can be improved conveniently according to the present invention are polymers and copolymers of aliphatic monoolefins containing 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, linear low density polyethylene, polypropylene, crystalline ethylenepropylene copolymer, poly(1-butene), vinyl cyclohexane, 1-hexene, 1-octene, and polymethylpentene. The polyolefins of the present invention may be described as basically linear, regular polymers that may optionally contain side chains such as are found, for instance, in conventional, low density polyethylene.

Other polymers that may benefit from the nucleation and clarification properties of the sorbitol acetals of the present invention include polyethylene terephthalate, polybutylene terephthalate, and polyamides, among others.

The olefin polymer or copolymer used in the composition of the present invention is crystalline, and the diffraction of light caused by microcrystals contained in it is considered to be responsible for the deterioration of the transparency of the polymer. It is thought that the diacetal composition functions in the target polyolefin to reduce the size of the microcrystals thereby improving the transparency of the polymer.

The composition of the present invention can be obtained by adding a specific amount of the diacetal composition directly to the olefin polymer or copolymer, and mixing them by any suitable means. Alternatively, a concentrate containing as much as about 20 percent by weight of the diacetal composition in a polyolefin masterbatch may be prepared and be subsequently mixed with the resin. Furthermore, the inventive alditol derivatives (and other additives) may be present in any type of standard polyolefin additive form, including, without limitation, powder, prill, agglomerate, liquid suspension, and the like, particularly comprising dispersion aids such as polyolefin (e.g., polyethylene) waxes, stearate esters of glycerin, montan waxes, mineral oil, and the like. Basically, any form may be exhibited by such a combination or composition including such combination made from blending, agglomeration, compaction, and/or extrusion.

Other additives such as a transparent coloring agent or plasticizers (e.g., dioctyl phthalate, dibutyl phthalate, dioctyl sebacate, mineral oil, or dioctyl adipate), can be added to the composition of the present invention so long as they do not adversely affect the improvement of transparency of the product. It has been found that plasticizers such as those exemplified above may in fact aid in the improvement of the transparency by the diacetal composition.

With regard to other additives it may also be desirable to employ the diacetal compositions disclosed above in combination with other conventional additives having known transparency improving effects such as, for instance, para-*t*-butylbenzoic acid, its salts, low molecular weight waxy polypropylene and the like. It may even be desirable to provide the particular diacetal compositions of the present invention in the polyolefin composition in combination with the previously described dibenzylidene sorbitol additive disclosed in U.S. Pat. Nos. 4,016,118 to Hamada et al., 5,049,605 to Rekers, and the like. In such applications, generally at least about 10 percent, preferably about 25 percent, or even about 50 percent or more of the clarity improving component will be the diacetal compositions of the present invention, with the remainder being comprised of other known clarifying agents, plasticizers, etc.

The compositions of the present invention may be obtained by adding the desired inventive asymmetric compounds or reaction product compositions to the polymer or copolymer and merely mixing the resultant formulation by any suitable means. The composition may then be processed and fabricated by any number of different techniques, including, without limitation, injection molding, injection blow molding, injection stretch blow molding, injection rotational molding, extrusion, extrusion blow molding, sheet extrusion, film extrusion, cast film extrusion, foam extrusion, thermoforming (such as into films, blown-films, biaxially oriented films), thin wall injection molding, and the like into a fabricated article.

Other additives may also be used in the composition of the present invention, provided they do not interfere with the primary benefits of the invention. It may even be advantageous to premix these additives or similar structures with the nucleating agent in order to reduce its melting point and thereby enhance dispersion and distribution during melt processing. Such additives are well known to those skilled in the art, and include plasticizers, lubricants, catalyst neutralizers, antioxidants, light stabilizers, colorants, other nucleating agents, and the like. Some of these additives may provide further beneficial property enhancements, including improved aesthetics, easier processing, and improved stability to processing or end use conditions.

In particular, it is contemplated that certain organoleptic improvement additives be added for the purpose of reducing the migration of degraded benzaldehydes from reaching the surface of the desired article. The term "organoleptic improvement additive" is intended to encompass such compounds and formulations as antioxidants (to prevent degradation of both

the polyolefin and possibly the target alditol derivatives present within such polyolefin), acid neutralizers (to prevent the ability of appreciable amounts of residual acids from attacking the alditol derivatives), and benzaldehyde scavengers (such as hydrazides, hydrazines, and the like, to prevent the migration of foul tasting and smelling benzaldehydes to the target polyolefin surface). Such compounds and formulations can be added in any amounts in order to provide such organoleptic improvements as needed. However, the amounts should not appreciably affect the haze results for the target polyolefin itself. Thus, lower amounts on the order of from about 20 ppm to about 2,000 ppm of the total polyolefin component are desired.

The compositions of the present invention are suitable as additives to improve the clarity of packaging materials and container materials for cosmetics, food-stuffs, and the like, because they give film, sheet, and other fabricated articles excellent transparency and physical properties.

Preferred Embodiments of the Invention

The following examples further illustrate the present invention but are not to be construed as limiting the invention as defined in the claims appended hereto. All parts and percents given in these examples are by weight unless otherwise indicated.

Asymmetric Compound Formation

EXAMPLE 1

Preparation of Asymmetric 3,4-Dichloro / 3,4-Dimethyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 3,4-dichlorobenzaldehyde (40 g, 0.2306 moles), 3,4-dimethylbenzaldehyde (37 g, 0.27 moles), 80 mL of methanol, and 2.5 g of water. *p*-Toluenesulfonic acid (3 g) was then added upon heating. The reaction then proceeded with increased temperature to reflux. Water was removed continuously from the Dean-Stark trap, and additional solvent was added as needed. After 6 hours, the reaction mixture was cooled and neutralized with 3.3 g of KOH in methanol (40 mL). 500 mL of water was then added, and the cyclohexane layer was then removed azeotropically, producing a residual white solid which was then filtered. The white solid was then washed with water, hot methanol, and oven dried. The product was produced in 91% yield, comprising about

63% of 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol, 25% of 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol, and the remainder (12%) of 1,3:2,4-bis(3,4-dichlorobenzylidene) sorbitol (as determined through Infrared Spectroscopy, Gas Chromatography/Mass Spectrometry, ^{1}H NMR, and C^{13} NMR, all collectively hereinafter referred to as "standard analyses"). DSC analysis of the solid @ 20°C/min showed melting transitions at about 266-268°C.

EXAMPLE 2

Preparation of Asymmetric 3,4-dichlorobenzylidene/ 6-tetrahydronaphthylidene sorbitol

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 moles), 700 mL of cyclohexane, 40.3g of 3,4-dichlorobenzaldehyde (0.2306 moles), 36.9 of 6-formyltetralin (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 100 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction became very thick and additional solvent was added as needed. After about six hours, the reaction was cooled, neutralized with potassium hydroxide, and filtered. The wet cake was washed thoroughly with water and methanol, dried in a vacuum oven at 110°C to give 72.6g (61%) of a white powder. The DBS purity was about 99% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(6-tetrahydronaphthylidene) sorbitol and 1,3-O-(6-tetrahydronapthylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol (60.4%), 1,3:2,4-bis(6-tetrahydronaphthylidene) sorbitol (25%), and 1,3:2,4-bis(3,4-dichlorobenzylidene) sorbitol (12.6%). DSC analysis of the solid @ 20°C/min showed melting transitions at 255.8-256.7°C.

EXAMPLE 3

Preparation of Asymmetric 3,4-Difluoro / 3,4-Dimethyl [50/50] DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 40.4g of 3,4-difluorobenzaldehyde (0.2306 moles), 30.93g of 3,4-dimethylbenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 100 mL of methanol. The reaction was stirred and heated under

reflux with removal of water through the Dean Stark trap. The reaction became very thick and additional solvent was added as needed. After about six hours, the reaction was cooled, neutralized with potassium hydroxide, and filtered. The wet cake was washed thoroughly with water and methanol, dried in a vacuum oven at 110°C to give 78.29g of a white powder. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(3,4-difluorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-difluorobenzylidene) sorbitol (60.7%), 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (21.2%), and 1,3:2,4-bis(3,4-difluorobenzylidene) sorbitol (18.0%). DSC analysis of the solid @ 20°C/min showed a melting transition range of 226-236°C.

EXAMPLE 4

Production of 3,4-dimethoxy/ 3,4-dichloro [50/50] DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 3,4-dimethoxybenzaldehyde (38 g, 0.2306 moles), 3,4-dichlorobenzaldehyde (40 g, 0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction became very thick and additional solvent was added as needed. After about six hours, the reaction was cooled, neutralized with potassium hydroxide, and filtered. The wet cake was washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give a white solid. Standard analyses of the material indicated that it consisted of about 52% of a mixture of 1,3-O-(3,4-dimethoxybenzylidene):2,4-O-(3,4-dichlorobenzylidene) sorbitol and 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethoxybenzylidene) sorbitol, and about 48% of 1,3:2,4-bis(3,4-dichlorobenzylidene) sorbitol, with no 3,4-dimethoxy DBS present. DSC analysis of the solid @ 20°C/min showed a melting transition range of 250-252 °C.

EXAMPLE 5

Production of 3,4-dichlorobenzylidene/5-indanylidene [50/50] DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with sorbitol (25.2 g, 0.138 moles), ice (23.6 g), and concentrated HCl (44.5 g). After fifteen

minutes of stirring, 24.2 g (0.139 moles) of 3,4-dichlorobenzaldehyde and 5-formylindan (18.5 g, 0.138 moles) were added as a mixture. A solution of cold water (200 mL) and KOH (72.0 g) was then added after 48 hours of further stirring. The resultant solids were then filtered, washed in hot water and hot methanol and vacuum-dried. Standard analyses showed the product to be 98% pure in asymmetrical diacetals. The product distribution could not be accurately determined due to the apparent similar volatility of the analytes. DSC analysis of the solid @ 20°C/min showed a melting transition range of 256-258 °C.

EXAMPLE 6

Production of 4-nitro/ 3,4-dimethyl [50/50] DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 25.4 g of D-sorbitol (0.139 moles), 15.4 g of water, and 34.8 g of concentrated HCl with stirring. Subsequently, 20.8 g (0.138 moles) of 4-nitrobenzaldehyde and 18.5 g (0.138 moles) of 3,4-dimethylbenzaldehyde were charged as a mixture and added to the homogenous mixture. A solid block of material formed within one hour of reaction and stirring was impossible. 200 mL of cold water and 56.2 g of KOH were then added permitting filtering of the resultant solids. The yellow filtrate measured a pH of about 14. The remaining solids were then washed with 300 mL of hot water and then 200 mL of hot methanol yielding a tan solid of 4-nitro/3,4-dimethyl asymmetric DBS (46.5 g) mixture. The components of this mixture were determined to be (through standard analyses) 15.1% 3,4-dimethyldibenzylidene sorbitol, 18.9% 4-nitrodibenzylidene sorbitol, and 62.4% mixed asymmetrics [1,3-O-(4-nitrobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene:2,4-O-(4-nitrobenzylidene) sorbitol]. The melting transition was found to be 224-227 °C by DSC analysis.

EXAMPLE 7

Production of asymmetric 4-nitro/3,4-methylenedioxy DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 25.2 g of sorbitol (0.138 mole)and 34.7 g of concentrated HCl. Subsequently, 21.0 g (0.139 moles) of 4-nitrobenzaldehyde and 20.9 g (0.139 moles) of piperonal (3,4-methylenedioxybenzaldehyde) were charged as a mixture and added to the homogenous

mixture. After two hours the reaction mixture turned yellow and some began to adhere to the sides of the flask. After seven more hours of such mixing, 200 mL of cold water and 56.8 g of KOH were then added and stirred for another 8 hours. Subsequently, the resultant solids were then collected, washed (in boiling water and boiling methanol) and filtered. The yellow-green filtrate measured a pH of about 14. This procedure yielded about 28 g of the 4-nitro/3,4-methylenedioxy asymmetric DBS mixture. The components of this mixture were determined to be (through standard analyses) 9.06% bis(3,4-methylenedioxybenzylidene) sorbitol, 16.63% bis(4-nitrobenzylidene) sorbitol, and 74.31% mixed asymmetrics [1,3-O-(4-nitrobenzylidene):2,4-O-(3,4-methylenedioxybenzylidene) sorbitol and 1,3-O-(3,4-methylenedioxybenzylidene):2,4-O-(4-nitrobenzylidene) sorbitol]. The melting transition was found to be 194-204°C by DSC analysis.

EXAMPLE 8

Preparation of Asymmetric 3,4-Dichloro / 3,4-Dimethyl DBX

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 40.00g of xylitol (0.263 moles), 600 mL of cyclohexane, 46g of 3,4-dichlorobenzaldehyde (0.263 moles), 35.2g of 3,4-dimethylbenzaldehyde (0.263 moles), 3.00g of p-toluenesulfonic acid, and 100 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction became very thick and additional solvent was added as needed. After about six hours, the reaction was cooled, neutralized with potassium hydroxide, and filtered. The wet cake was washed thoroughly with water and cyclohexane and dried in a vacuum oven at 110°C to give 108.9g (98%) of asymmetric 3,4-dichloro / 3,4-dimethyl DBX. The purity was determined to be 98% through gas chromatography analysis. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(3,4-dichlorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) xylitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dichlorobenzylidene) xylitol (78.7%), 1,3:2,4-bis(3,4-dimethylbenzylidene) xylitol (14.7%), and 1,3:2,4-bis(3,4-dichlorobenzylidene) xylitol (6.6%). The melting transition, as determined by melting point apparatus at a heating rate of 2 °C/minute, was found to be 248.2-251.9 °C.

EXAMPLE 9

Preparation of Asymmetric 4-Fluoro-3-methyl/3,4-Dimethyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 41.62g of sorbitol (0.2285 mole), 700 mL of cyclohexane, 31.56g of 4-fluoro-3-methylbenzaldehyde (0.2285 moles), 30.65g of 3,4-dimethylbenzaldehyde (0.2285 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 73.19g of Asymmetric 4-Fluoro-3-methyl / 3,4-Dimethyl [50/50] DBS. The purity was about 95% as judged by gas chromatography. Analyses of the material by gas chromatography/mass spectrometry, ^{1}H NMR, and C^{13} NMR (hereinafter "standard analyses") indicated that it consisted of a mixture of 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol (49.8%), 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (29.2%), and 1,3:2,4-bis(4-fluoro-3-methylbenzylidene) sorbitol (20.8%). DSC analysis of the solid @ 20°C/min showed multiple melting transitions at 232.9, 239.0, and 244.1°C.

EXAMPLE 10

Preparation of Asymmetric 4-Fluoro-3-methyl/4-Chloro DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 31.85g of 4-fluoro-3-methylbenzaldehyde (0.2306 moles), 32.41g of 4-chlorobenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 86.39g of Asymmetric 4-Fluoro-3-methyl / 4-Chloro [50/50] DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(4-chlorobenzylidene) sorbitol and 1,3-O-(4-

chlorobenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol (53.0%), 1,3:2,4-bis(4-chlorobenzylidene) sorbitol (27.6%), and 1,3:2,4-bis(4-fluoro-3-methylbenzylidene) sorbitol (19.4%). DSC analysis of the solid @ 20°C/min showed a peak melting transition at 224.6°C.

EXAMPLE 11

Preparation of Asymmetric 4-Fluoro-3-methyl/3-Fluoro-4-methyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 31.85g of 4-fluoro-3-methylbenzaldehyde (0.2306 moles), 31.85g of 3-fluoro-4-methylbenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 72.45g of asymmetric 4-Fluoro-3-methyl / 3-Fluoro-4-methyl [50/50] DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(3-fluoro-4-methylbenzylidene) sorbitol and 1,3-O-(3-fluoro-4-methylbenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol (57.8%), 1,3:2,4-bis(3-fluoro-4-methylbenzylidene) sorbitol (31.9%), and 1,3:2,4-bis(4-fluoro-3-methylbenzylidene) sorbitol (10.3%). DSC analysis of the solid @ 20°C/min showed a peak melting transition at 261.7°C.

EXAMPLE 12

Preparation of Asymmetric 4-Fluoro-3-methyl/benzaldehyde DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 31.85g of 4-fluoro-3-methylbenzaldehyde (0.2306 moles), 24.47g of benzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with

water and cyclohexane, dried in a vacuum oven at 110°C to give 60.39g of asymmetric 4-Fluoro-3-methyl / benzaldehyde [50/50] DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-benzylidene sorbitol and 1,3-O-benzylidene:2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol (50.9%), 1,3:2,4-bis(benzylidene) sorbitol (18.2%), and 1,3:2,4-bis(4-fluoro-3-methylbenzylidene) sorbitol (30.8%). DSC analysis of the solid @ 20°C/min showed multiple melting transitions at 200.9 and 211.2°C.

EXAMPLE 13

Preparation of Asymmetric 4-Fluoro-3-methyl/3-Chloro-4-fluoro DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 31.85g of 4-fluoro-3-methylbenzaldehyde (0.2306 moles), 36.56g of 3-chloro-4-fluorobenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 84.74g of asymmetric 4-Fluoro-3-methyl / 3-Chloro-4-fluoro [50/50] DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(4-fluoro-3-methylbenzylidene):2,4-O-(3-chloro-4-fluorobenzylidene) sorbitol and 1,3-O-(3-chloro-4-fluorobenzylidene):2,4-O-(4-fluoro-3-methylbenzylidene) sorbitol (52.8%), 1,3:2,4-bis(3-chloro-4-fluorobenzylidene) sorbitol (22.4%), and 1,3:2,4-bis(4-fluoro-3-methylbenzylidene) sorbitol (24.7%). DSC analysis of the solid @ 20°C/min showed a peak melting transition at 238.9°C.

EXAMPLE 14

Preparation of Asymmetric 4-Chloro-3-methyl/3-Chloro-4-methyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 53.46g of 4-chloro-3-methylbenzaldehyde (0.3458 moles), 17.82g of 3-chloro-4-methylbenzaldehyde (0.1152

moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 85.31g of asymmetric 4-Chloro-3-methyl / 3-Chloro-4-methyl [75/25] DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(4-chloro-3-methylbenzylidene):2,4-O-(3-chloro-4-methylbenzylidene) sorbitol and 1,3-O-(3-chloro-4-methylbenzylidene):2,4-O-(4-chloro-3-methylbenzylidene) sorbitol (38.2%), 1,3:2,4-bis(3-chloro-4-methylbenzylidene) sorbitol (5.3%), and 1,3:2,4-bis(4-chloro-3-methylbenzylidene) sorbitol (56.6%). DSC analysis of the solid @ 20°C/min showed a peak melting transition at 267.4°C.

EXAMPLE 15

Preparation of Asymmetric 3-Bromo-4-ethyl/3,4-dimethyl DBS

To an open reactor equipped with a mechanical stirrer was charged with 25g of sorbitol (0.14 mole), concentrated HCl (34.8g), and 0.38 g of dodecylbenzene sulfonate were charged to an open reaction vessel and stirred. After five minutes, 32 g of ground 2-(3-bromo-4-ethylphenyl)-1,3-dioxane (0.12 mol) and 3,4-dimethylbenzaldehyde (21 g; 0.16 mol) were mixed together with the initial formulation. After 8 hours of stirred reaction, 200 mL of cold water and KOH (72 g) were added. The resultant solids were then filtered and washed in basic water (800 mL with small amounts of KOH), then hot methanol (800 mL), then room temperature toluene (500 mL). Upon the addition of deionized water (400 mL) a white precipitate formed which was then dried by suction filtration and washed by stirring in methanol (800 mL), yielding 3-bromo-4-ethyl/3,4-dimethyl DBS mixtures as a light tan solid. Standard analyses of the material indicated that it consisted of a mixture of bis(3-bromo-4-ethylbenzylidene) sorbitol (10.3%), bis(3,4-dimethylbenzylidene) sorbitol (34.8%), and the remainder an asymmetric mixture of 1,3-O-(3-bromo-4-ethylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3-bromo-4-ethylbenzylidene) sorbitol. A melting transition was observed at 256.7-257.5°C when heated at 3°C/min on an Electrothermal 9300 Melting Point Apparatus.

EXAMPLE 16

Preparation of Asymmetric 3-Bromo-4-isopropyl/3,4-Dimethyl DBS

To an open reactor equipped with a mechanical stirrer was charged with 20.1g of sorbitol (0.137 mole), concentrated HCl (34.8g), and 0.34 g of dodecylbenzene sulfonate were charged to an open reaction vessel and stirred. After five minutes, 33.3 g of ground 2-(3-bromo-4-isopropylphenyl)-1,3-dioxane (0.117 mol) and 3,4-dimethylbenzaldehyde (21.0 g; 0.157 mol) were mixed together with the initial formulation. After 8 hours of stirred reaction, 200 mL of cold water and KOH (72 g) were added. The resultant solids were then filtered and washed in basic water (800 mL with small amounts of KOH), then boiling methanol (800 mL), yielding an asymmetric mixture of 3-bromo-4-isopropyl/3,4-dimethyl DBS as a light tan solid (6.9 g), exhibiting a melting point of 230.6-236.3°C. Standard analyses of the material indicated that it consisted of a mixture of bis(3-bromo-4-isopropylbenzylidene) sorbitol (1.8%), bis(3,4-dimethylbenzylidene) sorbitol (65.1%), and the remainder an asymmetric mixture of 1,3-O-(3-bromo-4-isopropylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3-bromo-4-isopropylbenzylidene) sorbitol.

EXAMPLE 17

Preparation of Asymmetric 3-Bromo-4-methyl/3,4-dimethyl DBS

To an open reactor equipped with a mechanical stirrer was charged with 25g of sorbitol (0.14 mole), concentrated HCl (34.8g), and 0.38 g of dodecylbenzene sulfonate were charged to an open reaction vessel and stirred. After five minutes, 30.3 g of ground 2-(3-bromo-4-methylphenyl)-1,3-dioxane (0.117 mol) and 21 g (0.157 mol) of 3,4-dimethylbenzaldehyde were mixed together with the initial formulation. After 8 hours of stirred reaction, 200 mL of cold water and KOH (72 g) were added. The resultant solids were then filtered and washed in basic water (800 mL with small amounts of KOH), then hot methanol (800 mL), then room temperature toluene (500 mL). The resultant solution was then poured into 400 mL of deionized water, thus precipitating a white solid which was then collected, dried by suction filtration, and washed by stirring in methanol (2 L), yielding 3-bromo-4-methyl/3,4-dimethyl DBS as a light tan solid. Standard analyses of the material indicated that it consisted of a mixture of bis(3-bromo-4-methylbenzylidene) sorbitol (15.2%), bis(3,4-dimethylbenzylidene) sorbitol (24.5%), and the remainder an asymmetric mixture of 1,3-O-(3-bromo-4-methylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol

and 1,3-O-(3,4-dimethylbenzlidene):2,4-O-(3-bromo-4-methylbenzylidene) sorbitol. A melting transition was observed at 271.9-274.5°C when heated at 3°C/min on an Electrothermal 9300 Melting Point Apparatus.

EXAMPLE 18

Preparation of 4-Chloro/3-bromo-4-isopropyl asymmetric DBS

To an open reactor equipped with a mechanical stirrer was charged with 12.6g of sorbitol (0.0692 mole), concentrated HCl (15 mL), 7.8 g of water, 15.7 g of 3-bromo-4-isopropylbenzylaldehyde (0.0692 mol), 9.69 g of 4-chlorobenzaldehyde (0.069 mol), and 0.2 g of dodecylbenzene sulfonate and the reactants were stirred together for 24 hours. A white solid precipitate formed during the reaction and was neutralized after the reaction was complete with a solution of KOH (10 g) in water (250 mL). The resultant solids were then collected by filtration and washed by stirring in boiling water then boiling cyclohexane to provide a 4-chloro/3-bromo-4-isopropyl asymmetric DBS mixture as a white powder exhibiting a melting transition of 212.5-218.9°. Standard analyses of the material indicated that it consisted of a mixture of bis(3-bromo-4-isopropylbenzylidene) sorbitol (14%), bis(4-chlorobenzylidene) sorbitol (45%), and the remainder an asymmetric mixture of 1,3-O-(3-bromo-4-isopropylbenzylidene):2,4-O-(4-chlorobenzylidene) sorbitol and 1,3-O-(4-chlorobenzylidene):2,4-O-(3-bromo-4-isopropylbenzylidene) sorbitol.

EXAMPLE 19

Preparation of Asymmetric 4-Fluoro / 3,4-Dimethyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 28.61g of 4-fluorobenzaldehyde (0.2306 moles), 30.93g of 3,4-dimethylbenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 72.96g of Asymmetric 4-fluoro / 3,4-dimethyl DBS. The purity was about 95% as judged by GC. Infrared Spectroscopy, Gas Chromatography/Mass Spectrometry, ^{1}H NMR, and C^{13} NMR, all

collectively hereinafter referred to as "standard analyses", of the material indicated that it consisted of a mixture of 1,3-O-(4-fluorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(4-fluorobenzylidene) sorbitol (50.8%), 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (27.3%), and 1,3:2,4-bis(4-fluorobenzylidene) sorbitol (21.5%). DSC analysis of the solid @ 20°C/min showed multiple melting transitions at 214.0 and 230.7°C.

EXAMPLE 20

Preparation of Asymmetric 3-Trifluoromethyl / 3,4-Dimethyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 40.15g of 3-trifluoromethylbenzaldehyde (0.2306 moles), 30.93g of 3,4-dimethylbenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 71.21g of Asymmetric 3-trifluoromethyl / 3,4-dimethyl DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(3-trifluoromethylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3-trifluoromethylbenzylidene) sorbitol (49.4%), 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (35.4%), and 1,3:2,4-bis(3-trifluoromethylbenzylidene) sorbitol (15.2%). DSC analysis of the solid @ 20°C/min showed multiple melting transitions at 220.8 and 250.3°C.

EXAMPLE 21

Preparation of Asymmetric 3-Fluoro/3,4-Dimethyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 28.61g of 3-fluorobenzaldehyde (0.2306 moles), 30.93g of 3,4-dimethylbenzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under

reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 72.02g of Asymmetric 3-fluoro / 3,4-dimethyl DBS. The purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(3-fluorobenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene)-2,4-O-(3-fluorobenzylidene) sorbitol (54.6%), 1,3:2,4-bis(3,4-dimethylbenzylidene) sorbitol (25.4%), and 1,3:2,4-bis(3-fluorobenzylidene) sorbitol (19.7%). DSC analysis of the solid @ 20°C/min showed multiple melting transitions at 216.3 and 235.1°C.

EXAMPLE 22

Preparation of Asymmetric 3-Fluoro / benzyl DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 32.76g of 3-fluoro-benzaldehyde (0.2306 moles), 30.93g of benzaldehyde (0.2306 moles), 3.00g of p-toluenesulfonic acid, and 210 mL of methanol. The reaction was stirred and heated under reflux with removal of water through the Dean Stark trap. The reaction becomes very thick and additional solvent is added as needed. After about six hours, the reaction is cooled, neutralized with potassium hydroxide, and filtered. The wet cake is washed thoroughly with water and cyclohexane, dried in a vacuum oven at 110°C to give 78.29g of Asymmetric 4-Fluoro / benzyl DBS. After washing with methanol, the purity was about 95% as judged by GC. Standard analyses of the material indicated that it consisted of a mixture of 1,3-O-(4-fluorobenzylidene):2,4-O-benzylidene sorbitol and 1,3-O-benzylidene:2,4-O-(4-fluorobenzylidene) sorbitol (42.3%), 1,3:2,4-bis(4-fluorobenzylidene sorbitol) (26.2%), and 1,3:2,4-bis(benzylidene) sorbitol (11.9%). A melting transition was observed at 193.7-195.2°C when heated at 3°C/min on an Electrothermal 9300 melting apparatus.

EXAMPLE 23

Preparation of 4-Fluoro/4-ethoxy asymmetric DBS

A one liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with

42.00g of sorbitol (0.2306 mole), 700 mL of cyclohexane, 29g of 4-fluorobenzaldehyde (0.23 moles), 35g of 3,4-ethoxybenzaldehyde (0.23 moles), 80 mL of methanol, and 2.5 g of water. The system was then flushed with argon and heated in an oil bath with stirring. Upon reaching a vapor temperature of 40°C, a solution of 3.00g of p-toluenesulfonic acid in 40 mL of methanol was added. The reaction was stirred and heated under reflux (about 120°C) and seeded with about 1.0 g of 3-ethoxy dibenzylidene sorbitol. The methanol/water layer was continuously drained from the trap as cyclohexane was returned to the reaction system. A white precipitate then formed after about 45 minutes. After subsequent heating to a vapor temperature of 70°C, glycerol (10 g) was then added. After attaining a vapor temperature then of 80°C, 100 mL of methanol was slowly added (with about 300 mL of cyclohexane added as well). A white precipitate then continued to form as became thicker. After attaining one last vapor temperature of 80°C, the reaction system was stirred at this elevated temperature for 1 hour. Subsequently, the reaction system was allowed to cool to room temperature, neutralized with potassium hydroxide in methanol, and washed in boiling water. The cyclohexane layer was then stripped and the remaining product was filtered to give the 4-fluoro/4-ethoxy asymmetric DBS mixture as a white solid. Standard analyses analysis of the material indicated that it consisted of a mixture of 1,3-O-(4-fluorobenzylidene):2,4-O-(4-ethoxybenzylidene) sorbitol and 1,3-O-(4-ethoxybenzylidene):2,4-O-(4-fluorobenzylidene) sorbitol (49.5%), 1,3:2,4-bis(4-fluorobenzylidene) sorbitol (24.5%), and 1,3:2,4-bis(4-ethoxybenzylidene) sorbitol (24.4%). DSC analysis of the solid @ 2°C/min showed multiple melting transitions at 211.3 and 212.4°C.

EXAMPLE 24

Preparation of 4-t-butyl/3,4-dimethyl DBS

D-Sorbitol (27 g, 0.15 mol), cyclohexane (500 mL), 4-*t*-butylbenzaldehyde (24 g, 0.15 mol), 3,4-dimethylbenzaldehyde (20 g, 0.15 mol), methanol (80 mL), water (2.5 g) and *p*-toluenesulfonic acid (3.0 g, 16 mmol) were added to a 2 L reaction kettle fitted with a mechanical stirrer, Dean-Stark trap with condenser and a thermometer. The system was flushed with argon and heated in an oil bath to reflux for 7 h. The methanol/water layer was continuously drained from the reaction system. Methanol was added as needed. The reaction mixture was cooled to room temperature and neutralized with KOH. The gray gel-like solid was filtered, washed three times with cyclohexane and dried in a vacuum oven to give mixture of 1,3;2,4-diacetal compounds determined through Infrared Spectroscopy, Gas

Chromatography/Mass Spectrometry, ^{1}H NMR, and C^{13} NMR, all collectively hereinafter referred to as "standard analyses", to be an asymmetric mixture of 1,3-O-(4-*t*-butylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene)-2,4-O-(4-*t*-butylbenzylidene) sorbitol (29%), 5% of bis(4-*t*-butylbenzylidene) sorbitol, and 66% of bis(3,4-dimethylbenzylidene) sorbitol, exhibiting a melting transition of 172-178°C.

EXAMPLE 25

Preparation of 3,4-dimethoxy/ 3,4-dimethyl DBS

A two liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42 g of sorbitol (0.23 mol), 2.5g of water, 80 mL of methanol, 38 g of 3,4-dimethoxybenzaldehyde (0.23 mol), 31g of 3,4-dimethylbenzaldehyde (0.23 mol), 3.3 g of *p*-toluenesulfonic acid and 700 mL of cyclohexane. The system was flushed with argon and heated in an oil bath to reflux for 5 h. The methanol/water layer was continuously drained from the reaction system. Methanol was added as needed. The reaction mixture was cooled to room temperature and neutralized with KOH. Water was then added and the cyclohexane layer was then stripped azeotropically, leaving a white solid collected by filtration. After washing with boiling water and boiling methanol, the result was a 3,4-dimethoxy/ 3,4-dimethyl asymmetric DBS mixture determined through standard analyses by gas chromatography to consist of an asymmetric mixture of 1,3-O-(3,4-dimethoxybenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-dimethoxybenzylidene) sorbitol (40%), and the remainder (60%) bis(3,4-dimethylbenzylidene) sorbitol. The melting transition was determined to be the range from 254.1-257.5°C.

EXAMPLE 26

Preparation of 4-isopropyl/ 3,4-dimethyl DBS

D-Sorbitol (27 g, 0.15 mol), cyclohexane (500 mL), 4-isopropylbenzaldehyde (22 g, 0.15 mol), 3,4-dimethylbenzaldehyde (20 g, 0.15 mol), methanol (80 mL) and water (2.5 g) were added to a 2 L reaction kettle fitted with a mechanical stirrer, Dean-Stark trap with condenser and a thermometer. The system was flushed with argon and heated in an oil bath to reflux for 7 h. The methanol/water layer was continuously drained from the reaction system. Methanol was added as needed. The reaction mixture was cooled to room

temperature and neutralized with KOH. The gel-like solid was filtered, washed one time with cyclohexane and dried in a vacuum oven to give mixture four 1,3;2,4-diacetal compounds determined through standard analyses to be an asymmetric mixture of 1,3-O-(4-isopropylbenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene)-2,4-O-(4-isopropylbenzylidene) sorbitol (39%), 10% of bis(4-isopropylbenzylidene) sorbitol, and 51% of bis(3,4-dimethylbenzylidene) sorbitol. The melting transition was determined to reside the range from 226 to 229°C.

EXAMPLE 27

Preparation of 2-naphthyl/ 3,4-dimethyl DBS sorbitol

A one liter reaction flask equipped with a mechanical stirrer was charged with 21.8 g of sorbitol (0.12 mol), 24 g of water, 46 mL of concentrated HCl, and 0.5 g of dodecylbenzene sulfonate. This mixture was stirred for about ten minutes, at which point a solution of 2-naphthaldehyde (15.6g, 0.1 mole) in 20 mL of water, and 3,4-dimethylbenzaldehyde (13.4g, 0.1 mole) was added. The mixture was stirred for 4 h. Cold water and KOH were then added to the reaction mixture. The solids were collected by vacuum filtration and washed with water and methanol to give a yellow solid deteremined through standard analyses to be a mixture of the two asymmetrics, 1,3-O-(2-naphthylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene)-2,4-O-(2-naphthylidene) sorbitol.

EXAMPLE 28

Preparation of 3,4-methylenedioxy/ 3,4-dimethyl DBS

A two liter four-necked cylindrical shaped reaction flask equipped with a Dean-Stark trap, condenser, thermometer, nitrogen inlet, and a mechanical stirrer was charged with 42g of sorbitol (0.23 mole), 2.5g of water, 80 mL of methanol, 35g of piperonal (0.23 moles), 31g of 3,4-dimethylbenzaldehyde (0.23 moles), 3.3 g *p*-toluenesulfonic acid and 700 mL of cyclohexane. The system was flushed with argon and heated in an oil bath to reflux for 5 h. The methanol/water layer was continuously drained from the reaction system. Methanol was added as needed. The reaction mixture was cooled to room temperature and neutralized with KOH. Water was then added and the cyclohexane layer was then stripped azeotropically, leaving a white solid collected by filtration. After washing with boiling water and boiling methanol, the result was a 3,4-methylenedioxy/ 3,4-dimethyl asymmetric DBS mixture

determined through standard analyses to consist of an asymmetric mixture of 1,3-O-(3,4-methylenedioxybenzylidene):2,4-O-(3,4-dimethylbenzylidene) sorbitol and 1,3-O-(3,4-dimethylbenzylidene):2,4-O-(3,4-methylenedioxybenzylidene) sorbitol (50%), 25% of bis(3,4-dimethylbenzylidene) sorbitol, and 25% of bis(3,4-methylenedioxybenzylidene) sorbitol. The melting transition was determined to reside in the range from 248.1-249.7°C.

Polyolefin Formation and Testing

One kilogram batches of target polypropylene were produced in accordance with the following table:

POLYPROPYLENE COMPOSITION 1 TABLE

Component	Amount
Polypropylene random copolymer flake (3% ethylene)(MF=12)	1000 g
Irganox® 1010, Primary Antioxidant (from Ciba)	500 ppm
Irgafos® 168, Secondary Antioxidant (from Ciba)	1000 ppm
Calcium Stearate, Acid Scavenger	800 ppm
Inventive Diacetal (and diacetal compositions)	as noted

The base resin (random copolymer, hereinafter "RCP") and all additives were weighed and then blended in a Welex mixer for 1 minute at about 1600 rpm. All samples were then melt compounded on a Killion single screw extruder at a ramped temperature from about 204° to 232°C through four heating zones. The melt temperature upon exit of the extruder die was about 246°C. The screw had a diameter of 2.54 cm and a length/diameter ratio of 24:1. Upon melting the molten polymer was filtered through a 60 mesh (250 micron) screen. Plaques of the target polypropylene were then made through extrusion into an Arburg 25 ton injection molder. The barrel molder was set at a temperature anywhere between 190 and 260°C, with a range of 210 to 240°C more preferred, and most preferably from about 220 to 230°C. The plaques had dimensions of about 51 mm X 76 mm X 1.27 mm, and were made in a mold having a mirror finish. The mold cooling circulating water was controlled at a temperature of about 25°C.

The same basic procedures were followed for the production of plaques of HP and LLDPE plastics but with the following composition:

LINEAR LOW DENSITY POLYETHYLENE COMPOSITION TABLE

Component	Amount
Dowlex® 2517 Linear Low Density Polyethylene (with Antioxidants and Acid scavengers already supplied)	1000 g
Sodium Stearate	500 ppm
Inventive Diacetal (and diacetal compositions)	as noted

The haze values were measured by ASTM Standard Test Method D1003-61 "Standard Test Method for Haze and Luminous Transmittance of Transparent Plastics" using a BYK Gardner XL-211 Hazemeter. Nucleation capabilities were measured as polymer recrystallization temperatures (which indicate the rate of polymer formation provided by the presence of the nucleating additive) by melting the target plaques and recording the temperature at which polymer re-formation occurs. An asterisk (*) denotes no measurements were taken.

EXPERIMENTAL TABLE 1

Results for Compounds Conforming with Formula (I), above

Test Plaque	(DBS Ex. # above)	Amount added (ppm)	Haze (%)	T_c (° C)
1	1	1000	37.9	*
2	1	1500	16.3	*
3	1	2000	9.1	*
4	1	2500	7.1	*
5	1	3000	6.5	113.1
6	1	3500	6.4	113.4
7	1	5000	6.3	113.3
8	2	1500	34.5	*
9	2	3500	11.1	110.7
10	3	1500	14.3	*
11	3	2500	9.0	*
12	3	3500	7.1	112.6
13	4	1500	29.5	*
14	4	3500	12.1	108.9
15	5	2500	11.9	*
16	5	3500	12.3	111.3
17	6	1500	14.2	*
18	6	3500	10.4	109.9
19	7	1000	22.0	*
20	7	1500	26.5	105.8
21	8	3500	48.0	103.0

Thus, the dipolar asymmetric DBS derivatives (within reaction product mixtures), exhibited favorable haze measurements and recrystallization temperatures in polypropylene plaques.

EXPERIMENTAL TABLE 2

Results for Compounds Conforming to Formula (II), above

Test Plaque No.	Additive (Example # from above)	Conc. (%)	Haze (%)	Resin Grade	Part Thick. (mil)	Polym. Recryst. Temp. (°C)
22	None	-----	55.8	RCP	50	96.1
23	9	.15	15.7	RCP	50	*
24	9	.20	8.6	RCP	50	*
25	9	.25	6.8	RCP	50	112.3
26	9	.35	6.4	RCP	50	112.5
27	None	-----	95.2	RCP	100	94.3
28	9	.15	44.6	RCP	100	*
29	9	.20	33.9	RCP	100	*
30	9	.25	31.1	RCP	100	*
31	9	.35	29.1	RCP	100	*
32	10	.25	9.7	RCP	50	114.5
33	10	.35	8.0	RCP	50	115.3
34	10	.50	7.3	RCP	50	115.7
35	11	.25	7.5	RCP	50	113.9
36	11	.35	6.6	RCP	50	113.5
37	11	.5	6.3	RCP	50	*
38	14	.15	25.0	RCP	50	108.5
39	14	.25	9.4	RCP	50	111.8
40	14	.35	6.1	RCP	50	112.3
41	14	.50	5.4	RCP	50	112.6
42	None	-----	90.1	LLDPE	50	99.6
43	10	.25	44.6	LLDPE	50	
44	10	.35	47.2	LLDPE	50	108.9
45	11	.25	51.0	LLDPE	50	
46	11	.35	51.7	LLDPE	50	108.4
47	12	.20	86.1	LLDPE	50	*
48	12	.25	59.6	LLDPE	50	*
49	12	.35	47.9	LLDPE	50	106.1
50	13	.20	81.7	LLDPE	50	*
51	13	.25	57.8	LLDPE	50	*
52	13	.35	46.8	LLDPE	50	*
53	14	.25	44.3	LLDPE	50	*
54	14	.35	48.6	LLDPE	50	*
55	14	.45	49.2	LLDPE	50	*
56	15	.3	12.9	RCP	50	*
57	15	.4	8.6	RCP	50	111.3
58	16	.3	11.3	RCP	50	*
59	16	.4	9.2	RCP	50	111.1
60	17	.3	11.1	RCP	50	*
61	17	.4	9.6	RCP	50	111.7
62	18	.35	23.8	RCP	50	105.0

Thus, the inventive asymmetric halogenated and alkylated alditol derivatives provided much improved optical and nucleation characteristics within the target thermoplastics as compared with the control.

EXPERIMENTAL TABLE 3

Results for Compounds Conforming to Formula (III), above

Test Plaque No.	Additive (from Example # above)	Conc. (%)	Haze (%)
63	None	-----	60.0
64	19	1500	17.1
65	19	2500	9.0
66	19	3500	7.5
67	20	1500	21.0
68	20	3500	7.2
69	21	1500	14.6
70	21	3500	6.1
71	23	1500	31.7
72	23	3500	26.1

Thus, the inventive single fluoro or fluorinated pendant group-containing asymmetric alditol derivatives provided much better characteristics within the target thermoplastics as compared with the control.

EXPERIMENTAL TABLE 4

Results for Compounds Conforming to Formula (IV) or (V), above

Test Plaque No.	Additive (from Example #)	Conc. (%)	Haze (%)
73	None	-----	70.0
74	24	1500	50.7
75	24	2500	22.6
76	24	3500	11.1
77	25	1500	12.2
78	25	3500	9.1
79	26	1500	25.7
80	26	2500	11.2
81	26	3500	7.9
82	27	1500	30.6
83	28	1000	16.2
84	28	2500	9.7
85	28	3500	16.6

Thus, such inventive asymmetric alditol derivatives provided improved clarification for polypropylene over the control without such additives present.

Gel Formation and Testing

Solid gels were also produced comprising the inventive alditol derivatives through recognized, simple methods. In particular, specific organic solvents were combined with the additives in certain concentrations and mixed thoroughly for between 5 and 120 minutes at an elevated temperature between about 100°F (77°C) and 300°F (149°C), preferably about 110°C, or at a temperature approaching, but not exceeding, the boiling point of the selected solvent (or solvents) to be gelled. The resultant solution was then poured into a mold and allowed to cool to room temperature to produce a gel stick. The solvents listed below are not intended to be exhaustive as to the potential types which may be utilized to form gels with the inventive 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.

EXPERIMENTAL TABLE 5

Gelling Results For Compounds Conforming to Formula (I), above

Ex. No.	Solvent	Additive – from Example # above	DBS Conc. (weight %)	Gel Formation (Y/N)	Gel Character (Hard/Soft)
86	1,2-Propanediol	1	1	Y	Soft
87	1,2-Propanediol	1	3	Y	Hard
88	2-Chlorotoluene	1	1	Y	Hard
89	2-Chlorotoluene	1	3	Y	Hard
90	1,2-Propanediol	8	1	Y	Soft
91	1,2-Propanediol	8	3	Y	Hard
92	2-Chlorotoluene	8	1	Y	Hard
93	2-Chlorotoluene	8	3	Y	Hard

Thus, the inventive asymmetric fluorine or fluorinated alditol derivatives provide excellent gelling capabilities for solvents, depending on their concentration within the target solvents.

EXPERIMENTAL TABLE 6

Gelling Results For Compounds Conforming to Formula (II), above

Ex. No.	Solvent	Additive – from Example # above	DBS Conc. (weight %)	Gel Formation (Y/N)	Gel Character (Hard/Soft)
94	1,2-Propanediol	10	1	Y	H
95	1,2-Propanediol	10	3	Y	H
96	1,3-Propanediol	10	1	Y	H
97	1,3-Propanediol	10	3	Y	H
98	2-Chlorotoluene	10	1	Y	H
99	2-Chlorotoluene	10	3	Y	H
100	Benzonitrile	10	1	Y	H
101	Benzonitrile	10	3	Y	H
102	1,2-Propanediol	11	1	Y	S
103	1,2-Propanediol	11	3	Y	S
104	1,3-Propanediol	11	1	Y	H
105	1,3-Propanediol	11	3	Y	H
106	2-Chlorotoluene	11	1	Y	S
107	2-Chlorotoluene	11	3	Y	H
108	Benzonitrile	11	1	Y	S
109	Benzonitrile	11	3	Y	H
110	1,2-Propanediol	12	1	Y	S
111	1,2-Propanediol	12	3	Y	H
112	1,3-Propanediol	12	1	Y	S
113	1,3-Propanediol	12	3	Y	H
114	2-Chlorotoluene	12	1	Y	S
115	2-Chlorotoluene	12	3	Y	H
116	Benzonitrile	12	1	Y	S
117	Benzonitrile	12	3	Y	H
118	1,2-Propanediol	14	1	Y	S
119	1,2-Propanediol	14	3	Y	H
120	1,3-Propandiol	14	1	Y	S
121	1,3-Propanediol	14	3	Y	H
122	2-Chlorotoluene	14	1	Y	S
123	2-Chlorotoluene	14	3	Y	H
124	Benzonitrile	14	1	Y	S
125	Benzonitrile	14	3	Y	H

Thus, the inventive asymmetric halogenated and alkylated alditol derivatives provide excellent gelling capabilities for solvents, depending on their concentration within the target solvents.

EXPERIMENTAL TABLE 7

Gelling Results For Compounds Conforming to Formula (III), above

Ex. No.	Solvent	Additive – from Example # above	DBS Conc. (weight %)	Gel Formation (Y/N)	Gel Character (Hard/Soft)
126	1,2-Propanediol	19	1	Y	Soft
127	1,2-Propanediol	19	3	Y	Hard
128	1,3-Propanediol	19	1	Y	Soft
129	1,3-Propanediol	19	3	Y	Hard
130	2-Chlorotoluene	19	1	Y	Hard
131	2-Chlorotoluene	19	3	Y	Hard
132	Benzonitrile	19	1	N	-----
133	Benzonitrile	19	3	Y	Hard
134	1,2-Propanediol	20	1	Y	Soft
135	1,2-Propanediol	20	3	Y	Hard
136	1,3-Propanediol	20	1	Y	Soft
137	1,3-Propanediol	20	3	Y	Hard
138	2-Chlorotoluene	20	1	Y	Hard
139	2-Chlorotoluene	20	3	Y	Hard
140	Benzonitrile	20	1	N	-----
141	Benzonitrile	20	3	Y	Hard

Thus, the inventive asymmetric fluorine or fluorinated alditol derivatives provide excellent gelling capabilities for solvents, depending on their concentration within the target solvents.

EXPERIMENTAL TABLE 8

Gelling Results For Compounds Conforming to Formulae (IV) or (V), above

Ex. No.	Solvent	Additive – from Example # above	DBS Conc. (weight %)	Gel Formation (Y/N)	Gel Character (Hard/Soft)
142	Propylene Glycol	24	1%	Y	Soft
143	Propylene Glycol	25	1%	Y	Soft
144	Propylene Glycol	28	1%	Y	Hard

Thus, the inventive asymmetric alditol derivatives provide acceptable gelling capabilities for certain solvents as well.

There are, of course, many alternative embodiments and modifications of the present invention which are to be included within the spirit and scope of the following claims.

CLAIMS

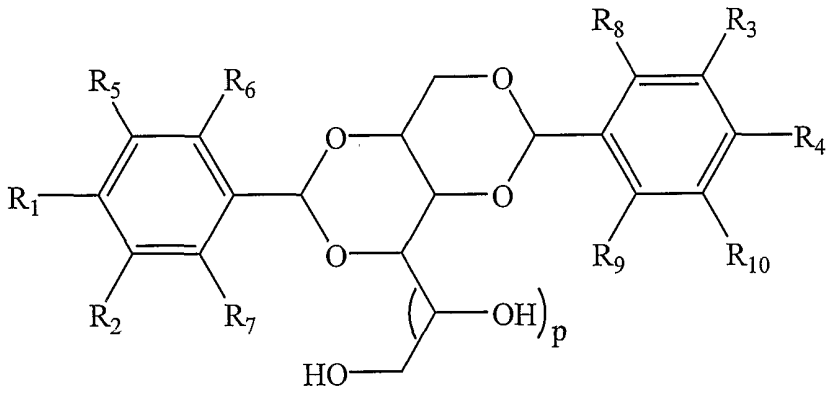
What is claimed is:

1. An asymmetric alditol di-acetal comprising at least two arylidene components wherein one of said arylidene components possesses either a single nitro pendant group or at least two electron drawing pendant groups and the other arylidene component must comprise at least two electron donating pendant groups.

2. An asymmetric alditol di-acetal comprising at least two arylidene components wherein one of said arylidene components at least possesses one halogen pendant group in either the 3- or 4- position and one pendant group selected from lower alkyl and lower alkoxy in either the 3- or 4- position.

3. An alditol di-acetal compound conforming with at least one of the Formulae (I)-(V):

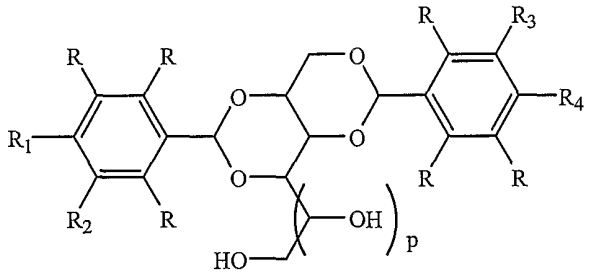
(I)



wherein p is 0 or 1, R_5, R_6, R_7, R_8, R_9, and R_{10} are each the same or different and are selected from electron donating groups, such as hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and electron withdrawing groups, such as halogens (meaning fluorine, chlorine, bromine, and iodine); R_1, R_2, R_3, and R_4 are the same or different and are selected from electron donating groups, such as hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, indan, tetralin, benzyl, substituted benzyl, or any two are combined to form a cyclic moiety, and electron withdrawing groups, such as nitro and halogens; with the first proviso that if one of said R_1, R_2, R_3, or R_4 groups is nitro, then no

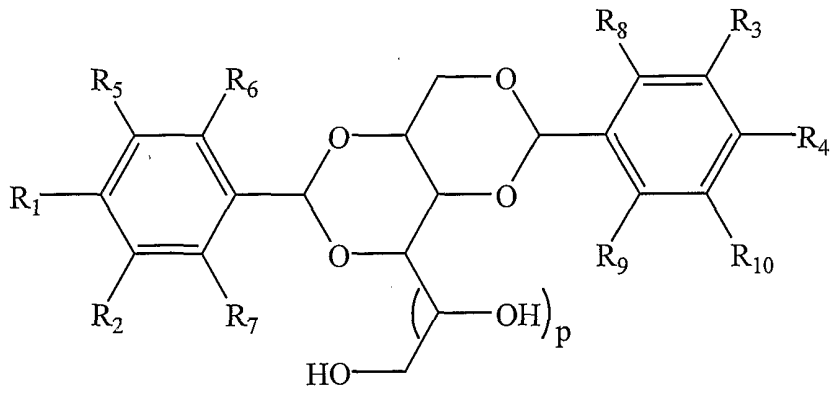
other nitro groups are present anywhere on the compound; with a second proviso that, unless s single nitro group is present, at least two electron withdrawing groups must be present and must be present as either the pair of R_1 and R_2 or the pair of R_3 and R_4 such that if one pair comprises such electron withdrawing groups, the other pair must comprise electron donating groups and the same ring system comprising such electron donating groups must not comprise any electron withdrawing groups;

(II)



wherein R is selected from hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and fluorine; R_1, and R_2, are selected from lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and halogens; R_3, and R_4 are selected from lower alkyl groups containing 1-4 carbon atoms and which together may form a carbocyclic ring containing up to 6 carbon atoms, lower alkoxy groups, halogens, and hydrogen; with the proviso that only one of R_1 and R_2 is halogen; and p is 0 or 1;

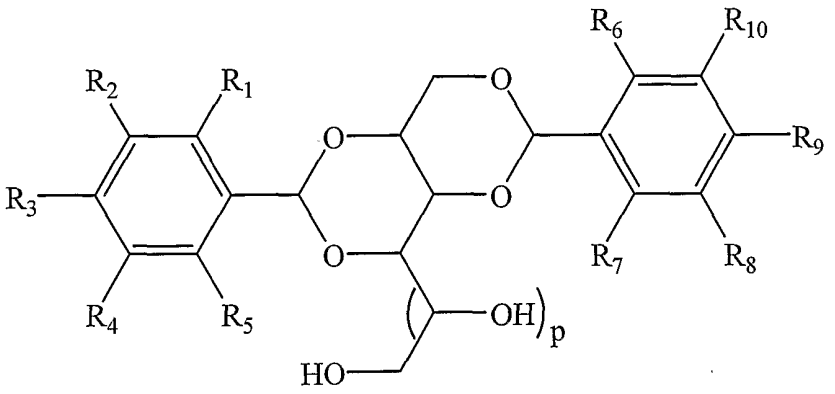
(III)



wherein p is 1 or 2, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are independently selected from the group consisting of hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, nitro, halogen, or any two adjacent groups may

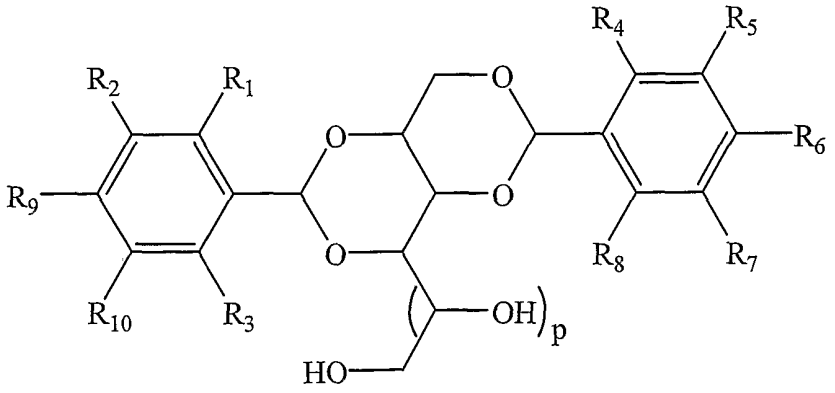
be combined to form a cyclic group; R_1, R_2, R_3, and R_4 are independently selected from the group consisting of hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, fluorine, and trifluoroalkyl groups containing 1-4 carbon atoms; with the proviso that either one of R_1 and R_2 or R_3 and R_4 is fluorine or trifluoroalkyl, as defined above, such that if one of said groups is a fluorine or trifluoroalkyl on a first ring system, then no other fluorines are present on the same first ring system, and, if said first ring system has only one fluorine pendant group in the 3- or 4-position, then the other ring system cannot have a single fluorine pendant group; and with a second proviso that if said first ring system comprises a fluorine in the 3- or 4-position, and an alkyl group in the 3- or 4-position, then the other ring system cannot exhibit the same pendant groups in the same positions as said first ring system;

(IV)



or

(V)



wherein for both (IV) and (V), p is 1 or 2, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are independently selected from the group consisting of hydrogen, alkyl groups containing 3-

6 carbon atoms, alkoxy groups containing 1-6 carbon atoms, phenyl, naphthyl, and substituted benzyl, or any two adjacent groups may be combined to form a cyclic group, wherein said cyclic group is selected from methylenedioxy, cyclohexyl, and cyclopentyl; with the provisos that at least two groups of R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are a group other than hydrogen, that at least one pendant group other than hydrogen is present on each ring, and that the entire compound is asymmetric.

4. A polyolefin composition comprising at least one compound defined within Claim 1.

5. A polyolefin composition comprising at least one compound defined within Claim 2.

6. A polyolefin composition comprising at least one compound defined within Claim 3.

7. A molten polyolefin composition comprising at least one polyolefin and at least compound defined within Claim 1.

8. A molten polyolefin composition comprising at least one polyolefin and at least compound defined within Claim 2.

9. A molten polyolefin composition comprising at least one polyolefin and at least compound defined within Claim 3.

10. A solid polyolefin article comprising at least one polyolefin component in solid polymerized form, and at least compound as defined in Claim 1.

11. A solid polyolefin article comprising at least one polyolefin component in solid polymerized form, and at least compound as defined in Claim 2.

12. A solid polyolefin article comprising at least one polyolefin component in solid polymerized form, and at least compound as defined in Claim 3.

13. A powdered composition comprising at least compound as defined in Claim 1.

14. A powdered composition comprising at least compound as defined in Claim 2.

15. A powdered composition comprising at least compound as defined in Claim 3.

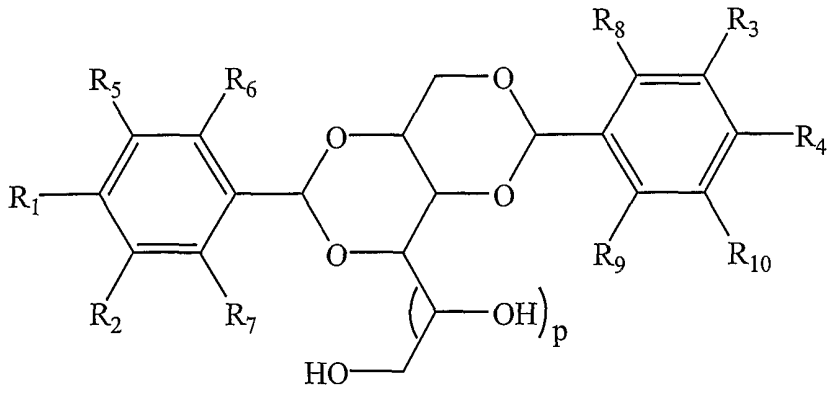
16. The polyolefin composition of Claim 4 wherein the proportion of the total amount of diacetal compounds within said polyolefin composition is from about 0.01 to about 2 percent by weight based upon the total weight of the composition.

17. The composition of claim 4, wherein said polyolefin comprises at least one aliphatic monoolefin.

18. The composition of Claim 17 where said at least one aliphatic monoolefin is selected from the group consisting of ethylene, propylene, vinyl cyclohexane, 1-butene, and methylpentene.

19. A solid gelled composition comprising at least one gelling agent compound conforming to at least one structure of Formulae (I)-(V)

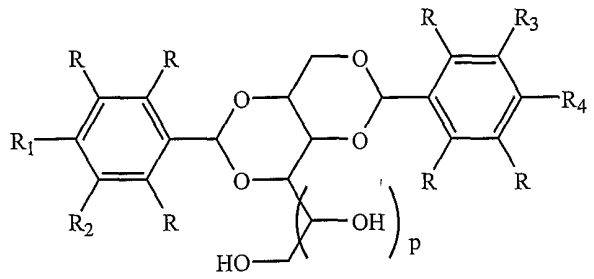
(I)



wherein p is 0 or 1, R_5, R_6, R_7, R_8, R_9, and R_{10} are each the same or different and are selected from electron donating groups, such as hydrogen, lower alkyl groups containing 1-4 carbon

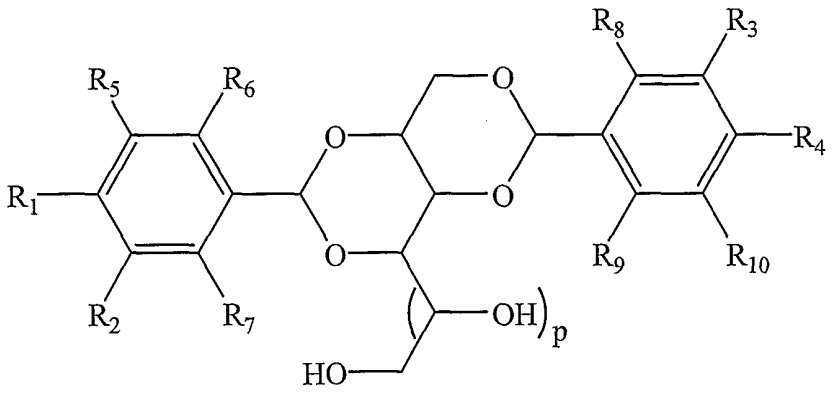
atoms, lower alkoxy groups, and electron withdrawing groups, such as halogens (meaning fluorine, chlorine, bromine, and iodine); R_1, R_2, R_3, and R_4 are the same or different and are selected from electron donating groups, such as hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, indan, tetralin, benzyl, substituted benzyl, or any two are combined to form a cyclic moiety, and electron withdrawing groups, such as nitro and halogens; with the first proviso that if one of said R_1, R_2, R_3, or R_4 groups is nitro, then no other nitro groups are present anywhere on the compound; with a second proviso that at least at least two electron withdrawing groups (other than the nitro group, above) must be present and must be present as either the pair of R_1 and R_2 or the pair of R_3 and R_4 such that if one pair comprises such electron withdrawing groups, the other pair must comprise electron donating groups and the same ring system comprising such electron donating groups must not comprise any electron withdrawing groups; and at least solvent for said gelling agent;

(II)



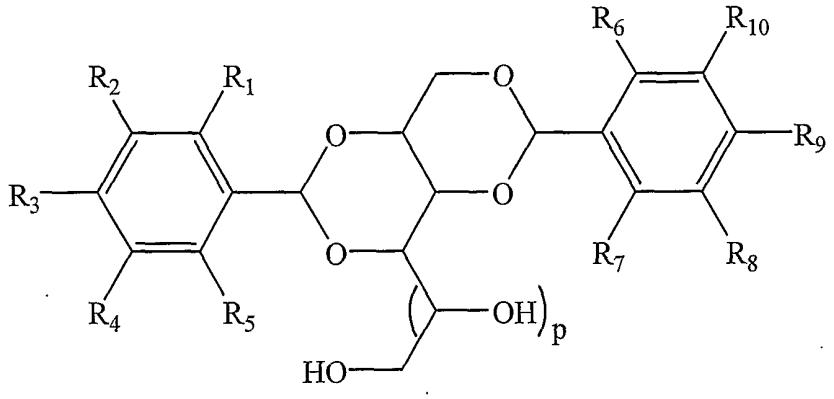
wherein R is selected from hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and fluorine; R_1, and R_2, are selected from lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, and halogens; R_3, and R_4 are selected from lower alkyl groups containing 1-4 carbon atoms and which together may form a carbocyclic ring containing up to 6 carbon atoms, lower alkoxy groups, halogens, and hydrogen; with the proviso that only one of R_1 and R_2 is halogen; and p is 0 or 1;

(III)



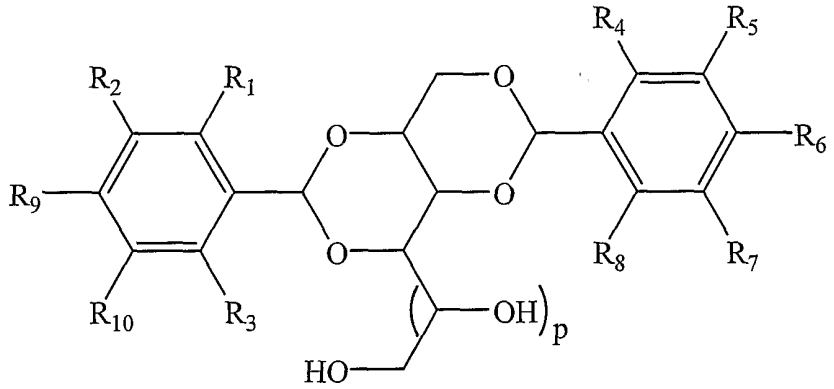
wherein p is 1 or 2, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are independently selected from the group consisting of hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, nitro, halogen, or any two adjacent groups may be combined to form a cyclic group; R_1, R_2, R_3, and R_4 are independently selected from the group consisting of hydrogen, lower alkyl groups containing 1-4 carbon atoms, lower alkoxy groups, fluorine, and trifluoroalkyl groups containing 1-4 carbon atoms; with the proviso that either one of R_1 and R_2 or R_3 and R_4 is fluorine or trifluoroalkyl, as defined above, such that if one of said groups is a fluorine or trifluoroalkyl on a first ring system, then no other fluorines are present on the same first ring system, and, if said first ring system has only one fluorine pendant group in the 3- or 4-position, then the other ring system cannot have a single fluorine pendant group; and with a second proviso that if said first ring system comprises a fluorine in the 3- or 4-position, and an alkyl group in the 3- or 4-position, then the other ring system cannot exhibit the same pendant groups in the same positions as said first ring system;

(IV)



or

(V)



wherein for both (IV) and (V), p is 1 or 2, R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are independently selected from the group consisting of hydrogen, alkyl groups containing 3-6 carbon atoms, alkoxy groups containing 1-6 carbon atoms, phenyl, naphthyl, and substituted benzyl, or any two adjacent groups may be combined to form a cyclic group, wherein said cyclic group is selected from methylenedioxy, cyclohexyl, and cyclopentyl; with the provisos that at least two groups of R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, and R_{10} are a group other than hydrogen, that at least one pendant group other than hydrogen is present on each ring, and that the entire compound is asymmetric.

20. A solid gel according to claim 19 wherein the solvent is selected from the group consisting of monohydric alcohols, polyhydric alcohols, propylene carbonate, propylene glycol, dipropylene glycol, DMSO, DMF, NMP, water, and mixtures thereof.

21. A solid gel according to claim 20 wherein the solvent is selected from the group consisting of propylene carbonate, methanol, ethanol, n-propanol, n-butanol, 2-methoxyethanol, 2-ethoxyethanol, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,4-butylene glycol, 1,2-butylene glycol, diethylene glycol, isopropanol, isobutanol, monomethyl ether, diethylene glycol monoethyl ether, 1,3-butylene glycol, 2,3-butylene glycol, dipropylene glycol, 2,4-dihydroxy-2-methylpentane, and mixtures thereof.

22. A solid gel according to claim 19 wherein the solvent is selected from aromatics, halogenated aromatics, nitrated aromatics, ketones, amines, nitriles, esters, aldehydes, and mixtures thereof.

23. A reaction product mixture comprising at least two isomeric compounds as defined by any of the structures of Formulae (I)-(V) in Claim 3 and at least one other reaction product, wherein said at least one other reaction product is a symmetrical alditol compound.

24. A reaction product mixture comprising at least two isomeric compounds as defined by any of the structures of Formulae (I)-(V) in Claim 3 and at least one other reaction product, wherein said at least one other reaction product is a symmetrical alditol compound.