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(54) Title: METHODS FOR SYNTHESIS OF LIQUID CRYSTALS

(57) Abstract: Novel platform molecules and polymerizable mesogens made therefrom; novel synthetic pathways for making such platform molecules and polymerizable mesogens.



WO 02/066493 A2

METHODS FOR SYNTHESIS OF LIQUID CRYSTALS**Priority Data**

The present application claims the benefit of the following provisional
5 applications, all filed January 23, 2001: Serial No. 60/263,387; Serial No.
60/263,392; Serial No. 60/263,388.

Government Rights Clause

The U. S. government has certain rights in this invention pursuant to grant
number NIDCR 1 P01 DE11688.

Field of the Invention

The application relates to new, less costly methods for making novel platform
molecules and polymerizable mesogens.

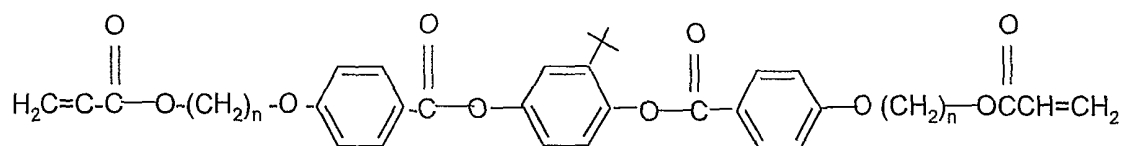
Background of the Invention

15 Photocurable resins which are transparent or translucent, radioopaque, have
good workability, and have good mechanical strength and stability are useful in
medical, dental, adhesive, and stereolithographic applications.

Low polymerization shrinkage is an important property for such resins. In
dental applications, the phrase "zero polymerization shrinkage" typically means that
20 the stresses accumulated during curing do not debond the dentin-restorative interface
or fracture the tooth or restorative, which can result in marginal leakage and microbial
attack of the tooth. Low polymerization shrinkage also is important to achieve
accurate reproduction of photolithographic imprints and in producing optical
elements.

25 Another advantageous property for such resins is maintenance of a liquid
crystalline state during processing. For comfort in dental applications, the resin

should be curable at “room temperature,” defined herein as typical ambient temperature up to body temperature. Preferred curing temperatures are from about 20 °C to about 37 °C. Mesogens which have been found to polymerize in a relatively stable manner at such temperatures are bis 1,4 [4'-(6'-methacryloxyhexyloxy) benzoyloxy] t-butylphenylene mesogens and their structural derivatives. These mesogens have the following general structure:



Unfortunately known synthetic methods for producing these mesogens are costly and have relatively low yields. As a result, the mesogens have enjoyed limited commercial use. Less costly synthetic methods are needed to produce the mesogens.

Summary of the Invention

A method for producing platform molecules comprising:

providing a first phenylene ring comprising a first functional group at a para-position to a second functional group;

15 providing a second phenylene ring comprising a third functional group at a para- position to a fourth functional group;

providing a third phenylene ring comprising a desired substituent and comprising and a first functionality at a para- position to a second functionality; and

20 reacting said first functional group with said first functionality, producing at least a first ester bond between said first phenylene ring and said third phenylene ring; and

reacting said third functional group with said third functionality, producing at

least a second ester bond between said second phenylene ring and said third phenylene ring, thereby producing platform molecules comprising a first terminal functionality at position para- to said first intervening ester bond and a second terminal functionality at a position para- to said second intervening ester bond, wherein at least one

5 functionality selected from the group consisting of said first terminal functionality and said second terminal functionality is other than a polymerizable group;

wherein, when both said first terminal functionality and said second

10 functionality are polymerizable groups, said desired substituent provides sufficient steric hindrance to achieve a nematic state at room temperature while suppressing crystallinity at room temperature.

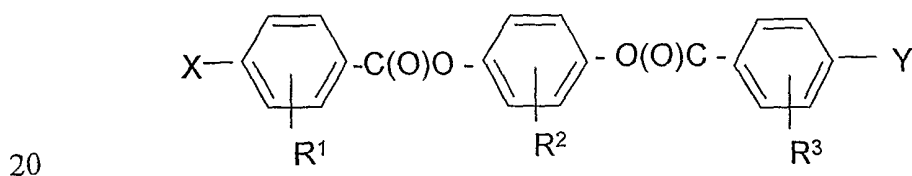
Detailed Description of the Invention

The application provides novel platform molecules, novel polymerizable

15 mesogens, novel methods for using the platform molecules, and novel intermediates and synthetic pathways for making the platform molecules and polymerizable mesogens.

The Mesogens

The mesogens of the present application have the following general structure:



wherein X and Y are selected from the group consisting of terminal functionalities

and polymerizable groups. In platform molecules, X and Y are terminal functionalities. In polymerizable mesogens, X and Y are polymerizable groups. Terminal functionalities and polymerizable groups are further defined below; and,

5 R^2 is a desired substituent, preferably a “bulky organic group,” defined herein as an organic group having a bulk greater than R_1 and R_3 , whereby, when both X and Y are polymerizable groups, said bulk is adapted to provide sufficient steric hindrance to achieve a nematic state at room temperature while suppressing crystallinity at room temperature. The result is effective rheology
10 - and workability at room temperature. Suitable R^2 groups generate asymmetry in the packing of the molecules, and include, but are not necessarily limited to alkyl groups having from about 1 to 6 carbon atoms and aryl groups. Preferred R^2 groups include, but are not necessarily limited to alkyl groups having from about 1 to about 4 carbon atoms and phenyl groups. More
15 preferred R^2 groups are methyl groups, t-butyl groups, isopropyl groups, secondary butyl groups, and phenyl groups. Most preferred R^2 groups are methyl groups and t-butyl groups; and

R^1 and R^3 are selected from groups less bulky than R^2 , preferably selected from the group consisting of hydrogen atoms and methyl groups, depending upon the
20 relative bulk of R^1 , R^3 , and R^2 .

As used herein, the phrase “terminal functionalities” refers to X and Y where the referenced molecules are platform molecules. “Terminal functionalities” are defined as protective groups and precursors to polymerizable groups, which generally comprise functionalities that readily react with “polymerizable groups” to form

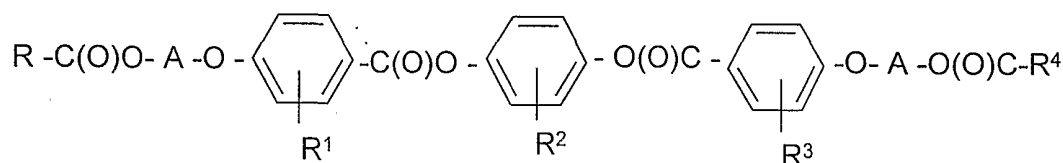
reactive ends. Suitable terminal functionalities independently are selected from the group consisting of hydroxyl groups, amino groups, sulfhydryl groups, halogen atoms, and "spacer groups", defined herein as selected from the group consisting of $H-(CH_2)_n-O-$ groups, $Cl(CH_2)_n-O-$ groups, $Br(CH_2)_n-O-$ groups, $I(CH_2)_n-O-$, wherein
5 n is from about 2 to about 12, preferably from about 2 to about 9, more preferably from about 2 to about 6, and most preferably 6, and the CH_2 groups independently can be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon atoms separate said oxygen or said ester group. Most preferred terminal functionalities are hydroxyl groups.

10 Where the mesogen is a polymerizable mesogen, X and/or Y are "polymerizable groups," defined as groups that may be polymerized by nucleophilic addition, free radical polymerization, or a combination thereof. Preferred polymerizable groups are polymerizable by Michael addition. Michael addition requires the addition of a nucleophile and an electron deficient alkene. Groups suitable for polymerization by
15 Michael addition include but are not necessarily limited to the examples found in A. Michael, *J. Prakt. Chem. [2]* **35**, 349 (1887); R. Connor and W. R. McClelland, *J. Org. Chem.*, **3**, 570 (1938); and C. R. Hauser, M. T. Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1959), all of which are incorporated by reference herein.

Examples of suitable polymerizable groups include, but are not necessarily
20 limited to substituted and unsubstituted alkenyl ester groups comprising a polymerizable unsaturated carbon-carbon bond, wherein said alkenyl group has from about 2 to about 12 carbon atoms, preferably from about 2 to about 9 carbon atoms, more preferably from about 2 to about 6 carbon atoms. In one embodiment, said substituted alkenyl ester groups comprise at least one halogen atom selected from the

group consisting of chlorine atoms, bromine atoms, and iodine atoms. Preferred alkenyl esters are acryloyloxy groups, methacryloyloxy groups, acryloyloxy alkoxy groups and methacryloyloxy alkoxy groups. More preferred polymerizable groups include, but are not necessarily limited to cinnamoyloxy groups, acryloyloxy groups, methacryloyloxy groups comprising an alkyl moiety having from about 2 to about 12 carbon atoms, thiolalkyloxy groups comprising an alkyl moiety having from about 2 to about 12 carbon atoms, preferably from about 2 to about 9, more preferably from about 2 to about 6, and most preferably 6 carbon atoms. Because asymmetry suppresses crystallinity while maintaining a nematic state, it is preferred for X and Y to be different groups.

Most preferred polymerizable mesogens are bis 1,4 [4'-(6'-(R,R⁴)-oxy-A-oxy)benzoyloxy] R²-phenylene mesogens. These mesogens have the following general structure:



This structure is similar to the structure of the platform molecules except that X and Y are replaced by polymerizable groups wherein:

A is selected from the group consisting of alkyl groups and methyl-substituted alkyl groups having from about 2 to about 12 carbon atoms, preferably having from about 2 to about 9 carbon atoms, more preferably having from about 2 to about 6 carbon atoms, and most preferably having about 6 carbon atoms; and

R and R⁴ are polymerizable groups, including but not necessarily limited to nucleophiles and groups comprising at least one electron deficient alkene.

Suitable nucleophiles include, but are not necessarily limited to ester groups, organic acid groups, amine groups, hydroxyl groups, and sulfhydryl groups.

5 More preferred polymerizable groups comprise electron deficient alkenes.

Suitable electron deficient alkenes independently are selected from the group consisting of substituted and unsubstituted alkenyl ester groups comprising a polymerizable unsaturated carbon-carbon bond, wherein said alkenyl group has from about 2 to about 12 carbon atoms, preferably about 6 carbon atoms.

10 In one embodiment, said substituted alkenyl ester groups comprise a halogen atom selected from the group consisting of chlorine atoms, bromine atoms, and iodine atoms. Preferred alkenyl esters are acryloyl groups and methacryloyl groups. Again, because asymmetry suppresses crystallinity while maintaining a nematic state, it is preferred for X and Y to be different groups.

15 One end of a polymerizable mesogen also may comprise a bridging agent, in which case R² may also be hydrogen or group less bulky than a methyl group, due to the inherent asymmetry of the dimer molecule. Dimers are discussed more fully below.

In a preferred embodiment, R² is either a t-butyl group or a methyl group, A is
20 a hexyl group, and one of R and R⁴ is selected from the group consisting of an acryloyl group and a methacryloyl group.

In a preferred embodiment, a proportion of X and/or Y (or R and/or R⁴) comprises a crystallization retardant. A "crystallization retardant" is defined as a substituent that retards crystallization of the monomers without suppressing the T_n.

>isotropic (the nematic to isotropic transition temperature). The proportion of X and/or Y (or R and/or R⁴) that comprises a crystallization retardant preferably is sufficient to suppress crystallinity of the mesogenic material, particularly at room temperature for dental applications, and to maintain flowability of the mesogenic material under the particular processing conditions. Suitable crystallization retardants include, but are not necessarily limited to halogen atoms. Exemplary halogen atoms are chlorine, bromine, and iodine, preferably chlorine. Typically, the proportion of the crystallization retardant required is about 3-50 mole%, more preferably 10-15 mole%, and most preferably about 14 mole% or less.

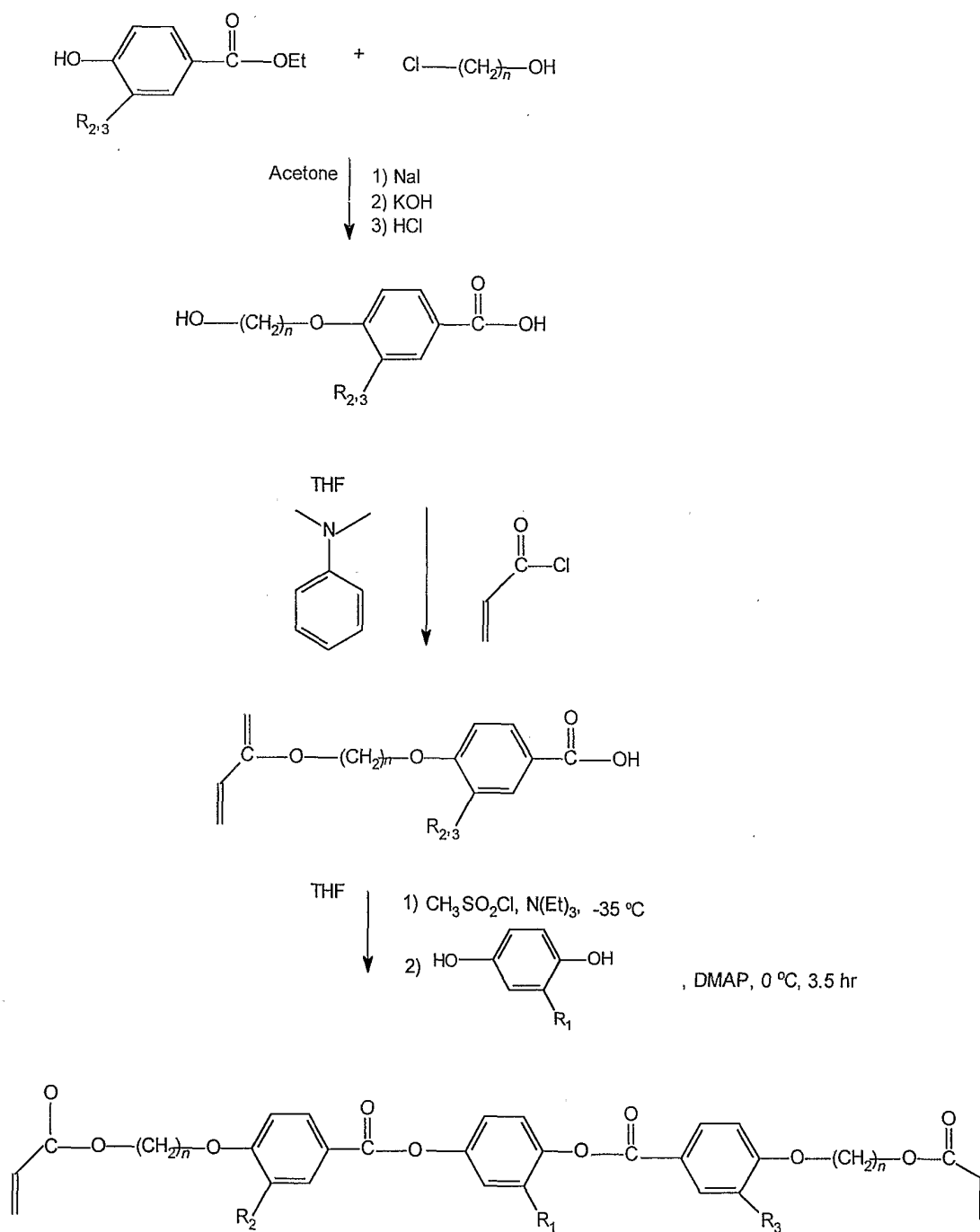
Depending on the sample preparation, the volumetric photopolymerization shrinkage of these materials at room temperature varies from about 0.9 to about 1.7%, which is a factor of 6-4X improvement over commercially available blends containing 2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy)phenylene] propane ("bis-GMA"). Preferably, the volumetric polymerization shrinkage is about 3 vol.% change or less, more preferably about 2 vol. % change or less.

Mesomers of higher temperature nematic stability are "mesogenic dimers," formed by reacting X and Y with opposite ends of a bridging agent. Examples of suitable bridging agents include, but are not necessarily limited to dicarboxylic acids (preferably α,ω -carboxylic acids) having from about 4 to about 12 carbon atoms, preferably from about 6 to about 10 carbon atoms, and oligodialkylsiloxanes preferably comprising alkyl groups having from about 1 to about 3 carbon atoms, most preferably methyl groups.

New Synthetic Pathways to Make the Mesogens

In the past, polymerizable mesogens having the foregoing structure were

synthesized by a multistep process ("Scheme 1"), as shown below:



Scheme 1.

- 5 In Scheme 1, molecular ends containing the outer aromatic groups and the alkyl groups were produced first and then coupled to the central aromatic group by diaryl

ester bonds. Specifically, the alkali phenoxide salt of p-hydroxybenzoic acid-ethyl ester nucleophile attacked the 6-hydroxy 1-chloro hexane with the aid of iodide catalyst to produce the 6-hydroxyhexyloxybenzoic acid (after hydrolysis of the ethyl ester) by a procedure that yielded at best 70% product. Although rather
5 straightforward, the commercial potential of this synthesis has been limited by the use of the 6-hydroxy 1-chlorohexane. The reaction is run in acetone over several days and requires significant workup. The reaction also produces only about a 40% overall yield, at best, and requires column separation to separate monosubstituted from disubstituted material

10 The present application provides new synthetic pathways that use relatively low cost materials to synthesize a central aromatic component comprising end groups that are easily reacted with the desired polymerizable groups. The methods are qualitative, produce high yields, the products are easily purified (preferably by crystallization), and many of the products are more stable than bisalkenes, which must
15 be stabilized against polymerization.

Brief Summary of the Processes

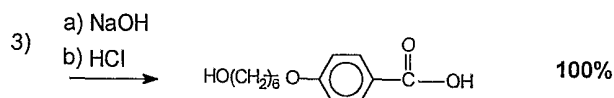
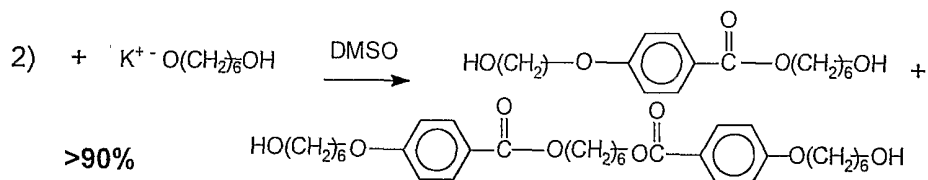
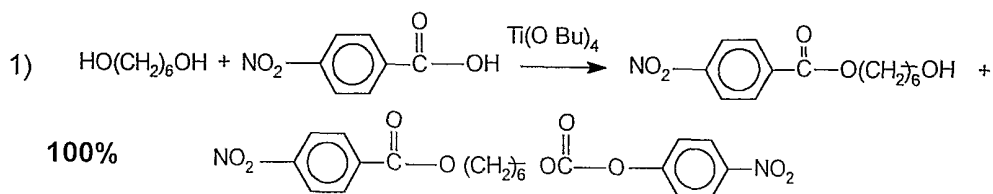
According to the present application, functionalities on a phenylene ring at para-positions (preferably hydroxyl groups) form ester linkages with one of two functionalities in para-positions on two other phenylene rings. The result is three-ring
20 platform molecules having terminal functionalities. One or both of the terminal functionalities may be coupled with polymerizable groups, preferably a nucleophile and/or an electron deficient alkene-containing group, to produce polymerizable mesogens.

-Preparation of Molecular Ends and Coupling to Central Aromatic Group

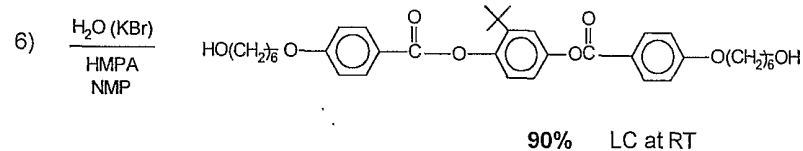
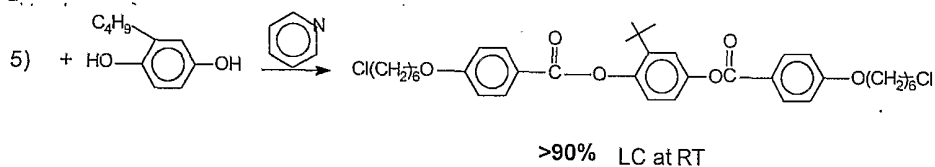
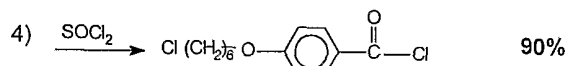
In a first embodiment (Scheme 2), the molecular ends of the mesogen (outer aromatic and alkyl groups) are prepared and coupled to the central aromatic group by diaryl ester bonds. This synthetic pathway is illustrated and described in detail below:

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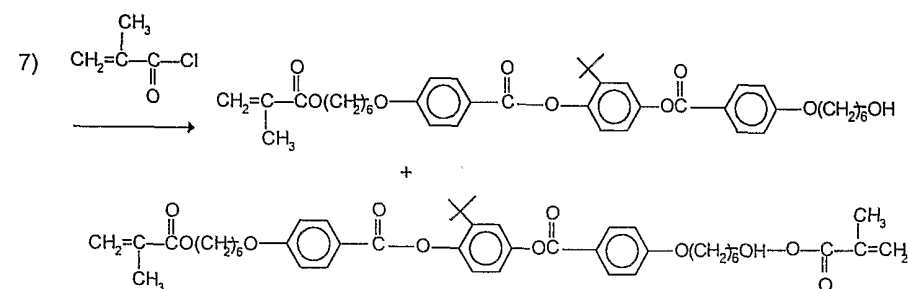
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Scheme 2.

Exemplary "platform molecules" are illustrated in (6), above.

To summarize Scheme 2, bis 1,4 [4''-(6'-chloroalkyloxy) benzoyloxy] R²-phenylene, preferably bis 1,4 [4''-(6'-chlorohexyloxy) benzoyloxy] t-butylphenylene,

is converted to the analogous bis ω -hydroxy or ω -hydroxy chloro compound. The hydroxy- compound (the platform molecule) may be terminated with one or more polymerizable groups. Preferred polymerizable groups are nucleophilic and electron deficient groups, most preferably independently selected from the group consisting of acryloyl groups, methacryloyl groups, and cinnamoyl groups.

More particularly:

(1) 4-nitrobenzoic acid is dissolved in an excess of the desired 1,6-dihydroalkane, preferably 1,6-dihydroxyhexane, in the presence of a suitable esterification catalyst. Suitable catalysts include, but are not necessarily limited to titanium alkoxides, tin alkoxides, sulfonic acid, and the like. A preferred catalyst is $\text{Ti}(\text{OBu})_4$. The dissolution occurs at atmospheric pressure at a temperature of from about 120 °C to about 140 °C, with stirring. If excess alcohol is used, the majority product is the 6-hydroxyalkyl ester of 4-nitrobenzoic acid plus some bis 1,6-(4-nitrobenzoyloxy) alkane, preferably 1,6-(4-nitrobenzoyloxy) hexane. The byproduct water is removed using suitable means, preferably under vacuum during the course of the reaction.

(2) One or more suitable solvents are added to the reaction mixture, along with alkali salts of diols. Suitable solvents include, but are not necessarily limited to aprotic solvents in which nucleophilic attack is preferred. Examples include, but are not necessarily limited to dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), dimethyl acetamide (DMAC), hexamethyl phosphonamide (HMPA). A preferred solvent is dimethylsulfoxide (DMSO), which is environmentally safe and relatively inexpensive. Suitable salts comprise cations effective to displace hydrogen and to produce the mono-cation salt of the alkanediol, preferably the nucleophilic

monosodium salt of hexanediol, in the presence of excess alkyl diol, preferably hexanediol. Preferred salts include, but are not necessarily limited to NaH or KOBu^t. The salt of the alkane diol, preferably hexane diol, then displaces the activated nitro group to produce 4-(1-hydroxyalkyloxy)benzoic acid (1-hydroxyalkyl ester) and some
5 of the dimeric compound. A preferred product is 4-(1-hydroxyhexyloxy)benzoic acid (1-hydroxyhexyl ester) and some of the dimeric compound. See N.Kornblum et al., J. Org. Chem., **41**(9), 1560 (1976) , incorporated herein by reference (nucleophilic displacement of nitro- group).

(3) The mixture from (2) is diluted with an aqueous base and heated to
10 completely cleave the aryl-alkyl ester to produce the desired 4-(6'-hydroxyalkyloxy)benzoic acid by precipitation subsequent to acidification. Suitable aqueous bases include, but are not necessarily limited to inorganic bases, a preferred base being aqueous sodium hydroxide. Suitable acids include, but are not necessarily limited to inorganic acids, a preferred acid being hydrochloric acid. In a
15 preferred embodiment, 4-(1-hydroxyhexyloxy)benzoic acid (1-hydroxyhexyl ester) is

diluted with aqueous sodium hydroxide and then acidified using hydrochloric acid to produce 4-(6'-hydroxyhexyloxy)benzoic acid. The supernatant contains sodium chloride and nitrite, which can be removed and recovered by vacuum evaporation of the solvent. In a preferred embodiment, the solvents evaporated are DMSO, 5 hexanediol and water, which may be discarded. DMSO and hexanediol can be recovered from the water phase by known distillation procedures.

(4) In a preferred embodiment, for small scale procedures, a quantitative conversion of the 4-(6'-hydroxyalkyloxy)benzoic acid to 4-(6'-chloroalkyloxy)benzoyl chloride is accomplished by mixing with thionyl chloride diluted in a suitable solvent, 10 preferably toluene, in the presence of pyridine base. In a preferred embodiment, 4-(6'-hydroxyhexyloxy)benzoic acid is converted to 4-(6'-chlorohexyloxy)benzoyl chloride in this manner. On a larger scale, the foregoing reaction is implemented with simple addition of SOCl_2 and venting of the byproduct SO_2 and HCl .

(5) The highly reactive 4-(6'-chloroalkyl)benzoyl chloride is coupled to a 15 hydroquinone bearing the desired bulky group, R^2 . In a preferred embodiment, 4-(6'-chlorohexyl)benzoyl chloride is mixed at room temperature with t-butyl hydroquinone in ether with pyridine, used as catalyst and as a base to take up released HCl , to form bis 1,4 [4''-(6'-hydroxyhexyloxy) benzoyloxy] t-butylphenylene. The reaction is quantitative and produces a high yield of the desired product. In addition, the bis 1,4 20 [4''-(6'-chloroalkoxy) benzoyloxy] R^2 -phenylene, preferably bis 1,4 [4''-(6'-chlorohexyloxy) benzoyloxy] t-butyl phenylene, is easily purified from the reaction mixture by crystallization. In addition, the bischloro compound is stable and need not be stabilized against polymerization (as must bis-alkene compounds).

- (6) The bischlorocompound is hydrolyzed to the platform molecule, preferably bis 1,4 [4''-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene, by simple heating in an aprotic solvent in the presence of water and potassium bromide [R.O. Hutchins and I.M. Taffer, J.Org. Chem, **48**, 1360 (1983)]. Again, the reaction is
- 5 quantitative with the product being purified by recrystallization. The reaction can be stopped at intermediate times to produce any desired mixture of monofunctional and difunctional alcohol molecules. In addition, the chloro-terminated molecules can be converted to the more reactive iodo-terminated species by simple exchange with NaI in acetone.
- 10 (7) The dialcohol or mixed alcohol/alkyl chloride is easily reacted with one or more polymerizable groups, preferably Michael addition reactants. In a preferred embodiment, one or more of the dialcohol ends is reacted with alkenyl chlorides to form reactive alkenyl esters, which can have any ratio of alkenyl ester, halide, or alcohol termini. The ratio can be adjusted to adjust the crosslink density and the
- 15 liquid crystal transition temperatures.

Selective Ether Cleavage

- In a preferred embodiment, 4-alkoxy benzoyl chloride, preferably commercially available 4-methoxy benzoyl chloride, is reacted with a hydroquinone substituted with a desired R² group to produce the corresponding aromatic ester, bis 1,4 [4-
- 20 alkoxybenzoyloxy] phenylene, preferably bis 1,4 [4-methoxybenzoyloxy] phenylene. The reaction takes place in the presence of an appropriate HCl scavenger and solvent. Suitable HCl scavengers include, but are not necessarily limited to aromatic and aliphatic amines, with a preferred HCl scavenger being pyridine. The pyridine also

may be used in combination with a trialkyl amines having from about 2-4 carbon atoms, preferably triethyl amine.

In a second "step," the alkoxy group is cleaved to result in a reactive hydroxyl group while leaving the aromatic ester and thus the triaromatic mesogen structure intact. See M. Node et al., J. Org. Chem., **45**, 4275 (1980)] (Figure 7a), incorporated herein by reference. Node suggests that the methyl ether of bis 1,4 [4-methoxybenzoyloxy] phenylene can be selectively cleaved in the presence of a nucleophile, preferably a thiol, and a Lewis acid, such as aluminum chloride, to produce bis 1,4 [4-hydroxybenzoyloxy] phenylene. [See M. Node et al., J. Org. Chem., **45**, 4275 (1980)] ("Node"), incorporated herein by reference. However, Node describes cleaving methyl ethers in the presence of aliphatic esters--not in the presence of aromatic esters. In initial experiments using the conditions described in Node, the more unstable aromatic esters underwent significant ester cleavage because the product complex remained in solution where additional reaction can occur.

Surprisingly, selective cleavage of the aliphatic ether in the presence of the aromatic esters was induced at low temperatures using much higher methyl ether concentrations than those described in Node. Using high concentrations of the ether and much lower concentrations of the nucleophile induced a "complex"-- containing the dihydroxy product with intact aromatic ester bonds--to precipitate from the reaction mixture at short reaction times as the complex was formed. The precipitated complex decomposed to the desired dihydroxy compound by reacting the complex with water and/or alcohol.

Suitable ethers for use in the reaction include, but are not necessarily limited to alkyl ethers, having from about 1 to about 8, preferably 1 to 4 carbon atoms. A

most preferred ether is methyl ether. Suitable nucleophiles for use in the reaction include, but are not necessarily limited to aliphatic thiols. Preferred nucleophiles are liquid alkanethiols, which typically have 11 carbon atoms or less. A most preferred nucleophile is ethane thiol.

5 Preferably, a minimum amount of thiol is used to dissolve aluminum chloride in the presence of the ether and a solvent. A most preferred embodiment uses at least 1 mole of thiol per mole of alkyl ether, preferably 2 moles of thiol per mole of alkyl ether. A most preferred embodiment uses 7 mmol of the methyl ether per ml of ethane thiol.

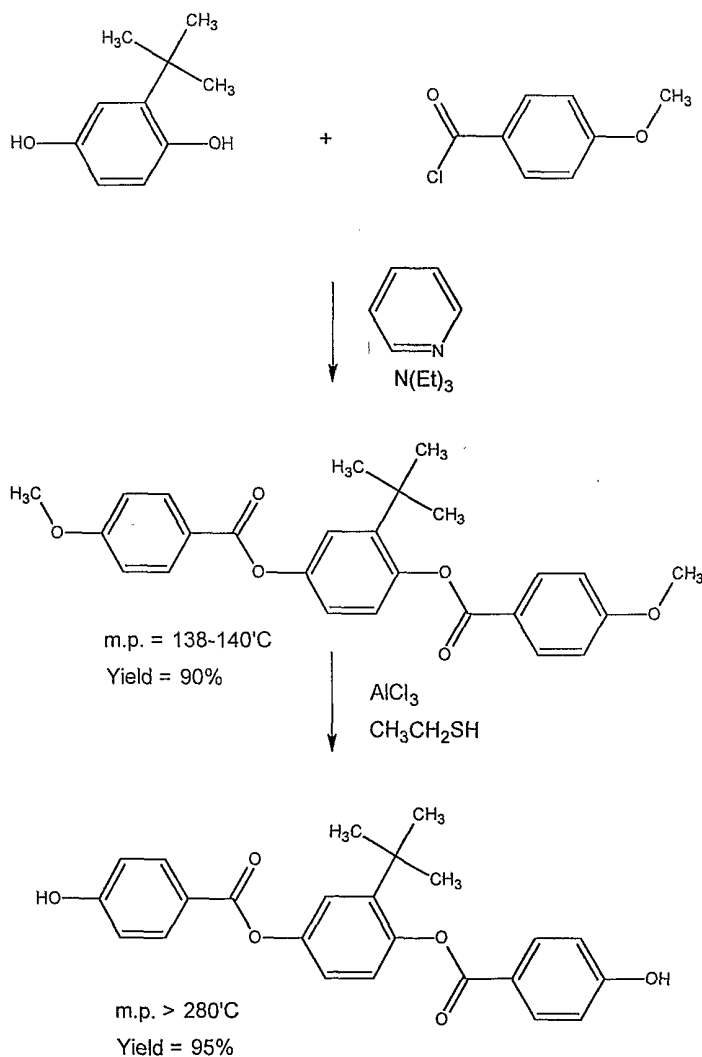
10 The aluminum chloride to ether ratio should be 4:1 or more, as this appears to be the ratio needed for complexation. At ratios of aluminum chloride to thiol of above 5, more of the complex will stay in the solution before saturation occurs thus resulting in aromatic ester cleavage and reduced yield. The use of less aluminum chloride will result in an incomplete cleavage of the methyl ether. The use of more
15 aluminum chloride, in excess of 4 to 1, has shown no effect in increasing the reaction rate, but slight excesses such as 4.5 to 1 can compensate for residual water in the system.

 Suitable solvents for use in the reaction are halogenated solvents, preferably chlorinated solvents, most preferably dichloromethane. The solvent concentration can
20 range from a molar excess of from about 3 to about 7, preferably about 5 or more, in relation to the nucleophile (thiol), as needed to keep the solution in a slurry as precipitate forms. However, dichloromethane above a 5 molar excess should be added slowly as the reaction proceeds since high initial concentration of the methylene chloride will hinder the reaction rate.

The reaction preferably is started under dry conditions at about 0 °C but can be allowed to warm to room temperature (~25 °C) as it proceeds. The reaction should not go above room temperature or ester cleavage can occur.

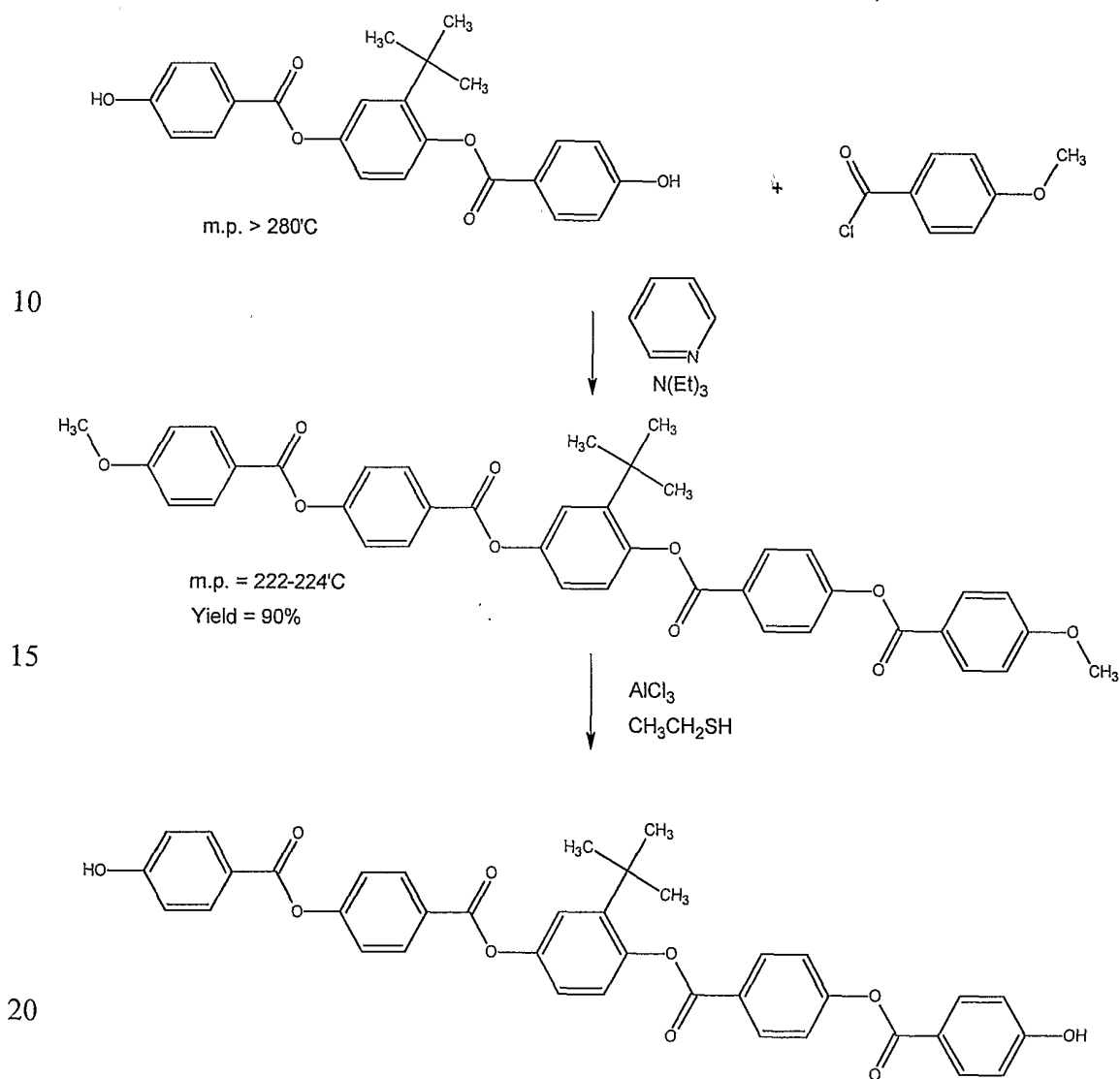
Upon increasing methyl ether concentration to 35X the concentrations used by
5 Node, the solubility limit of the product complex was exceeded, permitting the complex to crystallize out of the reaction mixture before the aromatic esters had an opportunity to cleave. Quantitative yields were obtained when the complex crystallized directly from the reaction mixture, effectively removing the molecule from further reaction that would form side products:

10



The diphenolic platform mesogens can be lengthened by reacting additional 4-methoxy benzoyl chloride with bis 1,4 [4'-methoxybenzoyloxy] t-butylphenylene to produce the dimethoxy compound with four or five aromatic rings, depending upon the reactant ratios. Cleavage with Lewis acid and thiol produces the respective

5 elongated diphenolic platform molecules:



The phenolic end group(s) are esterified by acyl chlorides, thus providing a route to polymerizable mesogens. For example, reaction of $C_0[H,TB,H](OH)_2$ with methacryloyl chloride formed the monoester which was coupled to bifunctional sebacoyl chloride to form an alkyl diester linked, methacrylate terminated liquid crystalline monomer, $\{C_0[H,TB,H](MeAcry)(O)\}_2(seb)$ with $T_{n \rightarrow I}$ of 145°C and a T_g of 25°C. This monomer had no tendency to crystallize since the synthesis yielded three different isomers with differing mutual orientation of t-butyl groups. The material is highly viscous, however, making processing close to room temperature, and thus T_g , somewhat inconvenient.

10 **Formation of Dimers**

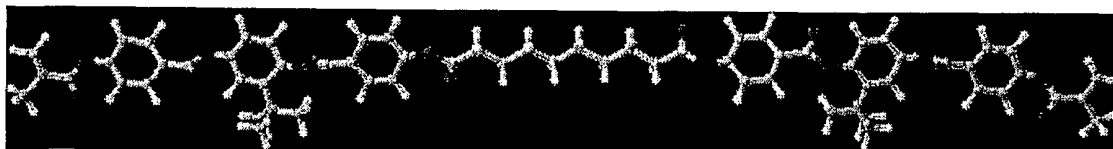
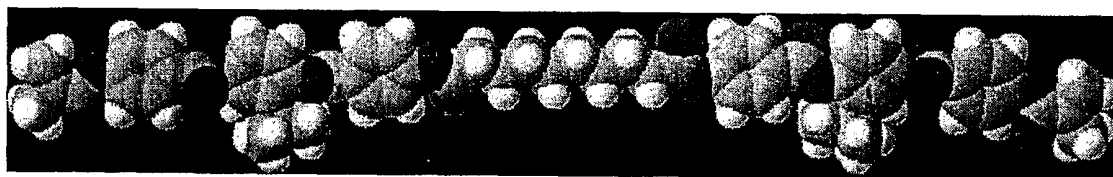
Preferred non-reactive dimeric and polymeric derivatives of $C_6[H,TB,H]$ type mesogenic cores are much more unlikely to crystallize [S. Lee et al., *Macromol.*, **27**(14), 3955 (1994)]. In addition, blends of non-reactive dimeric with monomeric derivatives ($C_6[H,TB,H](Me)_2$) generated a phase diagram with isotropic, isotropic + nematic and finally, at the lowest temperatures, a nematic phase. Adding polymer to the monomer substantially increases $T_{n \rightarrow n+I}$.

Briefly, in order to make the dimer molecule, a second mesogenic, platform molecule, 1,4 [4'-hydroxybenzoyloxy] t-butylphenylene, $C_0[H,TB,H](OH)_2$, is synthesized by coupling p-anisoyl chloride with t-butyl hydroquinone and then cleaving the methoxy end groups, as described above, preferably using ethanethiol and aluminum chloride. This molecule can be further extended by reaction with p-anisoyl chloride and the same methoxy cleavage reaction. Fully aromatic diphenol terminated mesogens of any length can be thus produced.

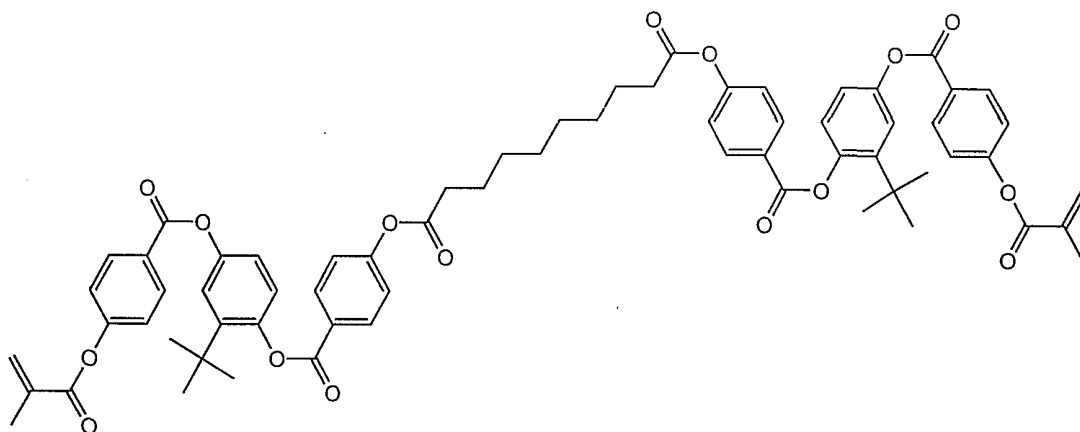
Reaction of $\text{C0[H,TB,H]}(\text{OH})_2$ with a less than stoichiometric amount of methacryloyl chloride forms the monoester and diester. The monoester and diester are washed away from the diphenol starting material with methylene chloride and the monoester is separated from the diester as an insoluble solid by diluting the methylene chloride solution into hexane.

The monoester can be coupled to bifunctional sebacoyl chloride to form an alkyl diester linked, methacrylate terminated liquid crystalline monomer, $\{\text{C0[H,TB,H]} (\text{MeAcry})(\text{O})\}_2 (\text{seb})$ with $T_{n \rightarrow I}$ of 145°C and a T_g of 25°C . This monomer has no tendency to crystallize since the synthesis yields three different isomers with differing mutual orientation of t-butyl groups. However, processing close to room temperature, and thus T_g , is inconvenient because of the high viscosity of the material.

The following is a ChemSketch 4 rendition of the minimum energy conformation of $\{\text{C0[H,TB,H]} (\text{MeAcry})(\text{O})\}_2 (\text{seb})$. As expected the most stable conformation is an extended form with a very high molecular length to width ratio which is likely to form high $T_{n \rightarrow I}$ liquid crystal monomers.



A minimum energy conformation of a preferred mesogenic dimer is decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester {C₀[H,TB,H] (MeAcry)(O) }₂ (seb):

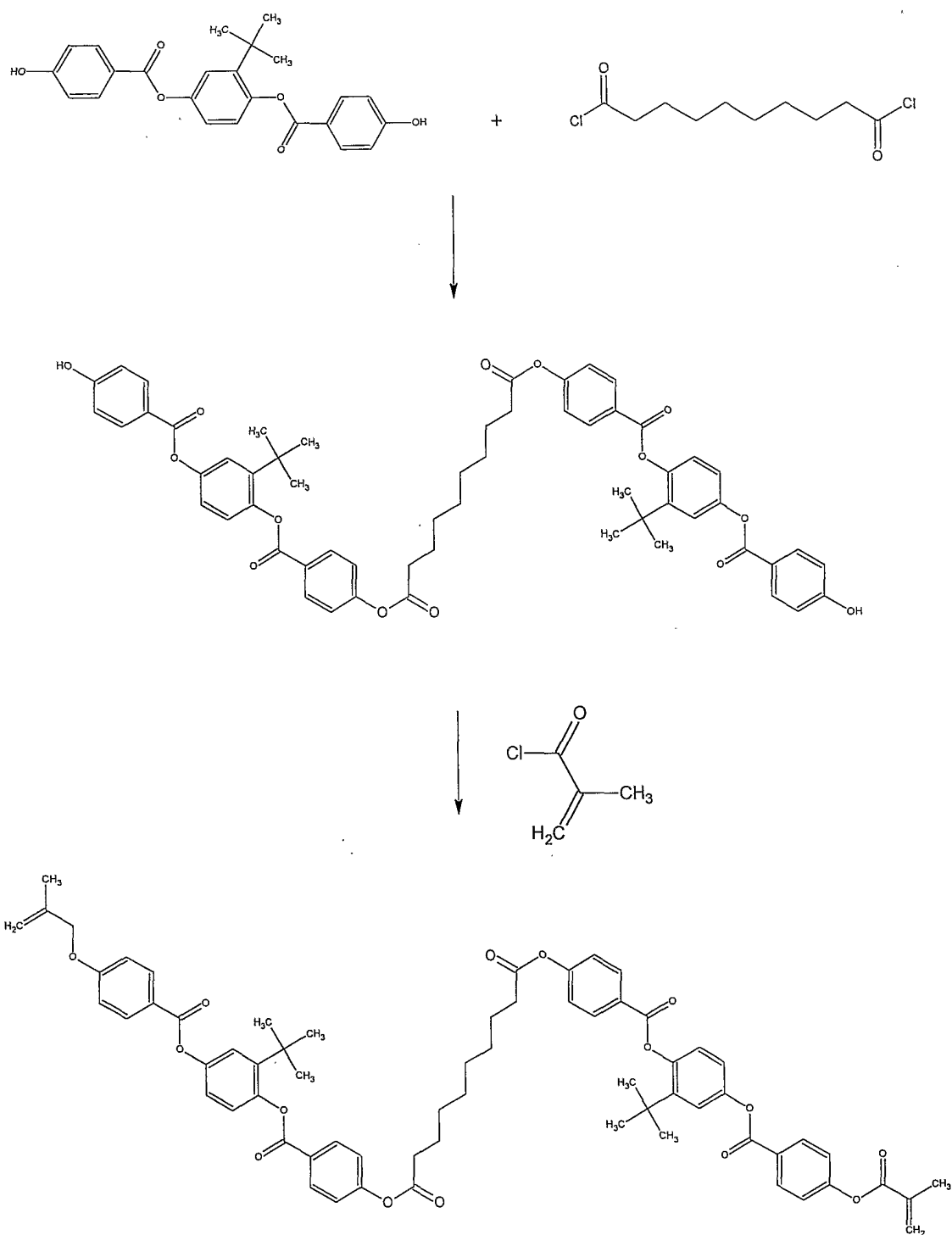


C₆₆H₆₆O₁₆
 Exact Mass: 1114.44
 Mol. Wt.: 1115.22
 C, 71.08; H, 5.97; O, 22.95

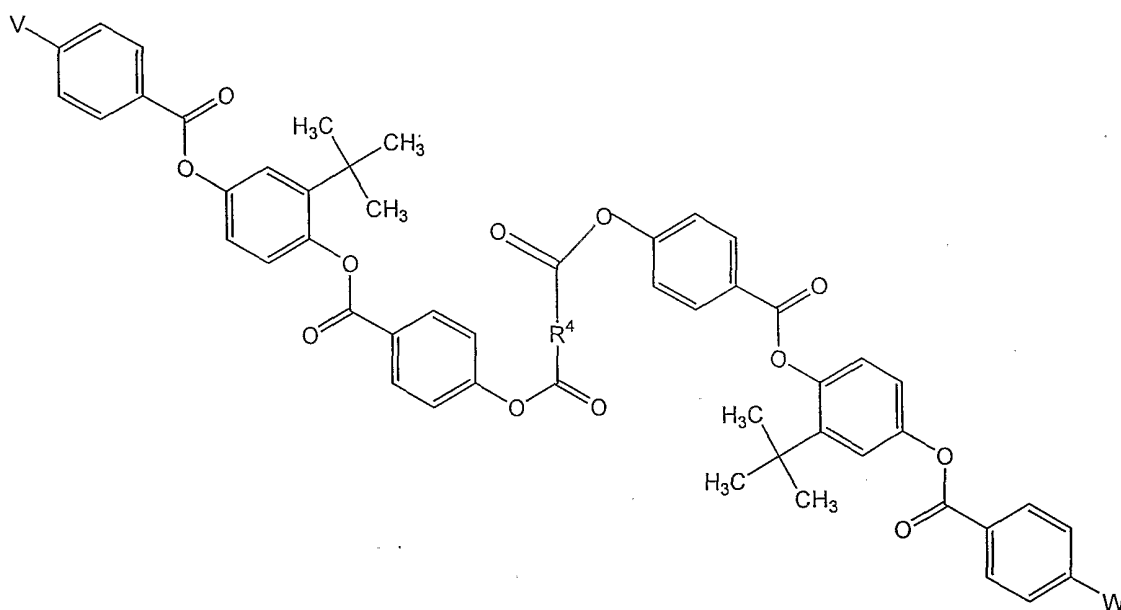
5

Alternately, the partially or completely methacryloylated or acryloylated versions of decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester and decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester are made as

10 illustrated below:



- 5 The first reaction product in the above figure is a novel alkylenedioic bis-(4-{2-alkyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester having the following general structure:



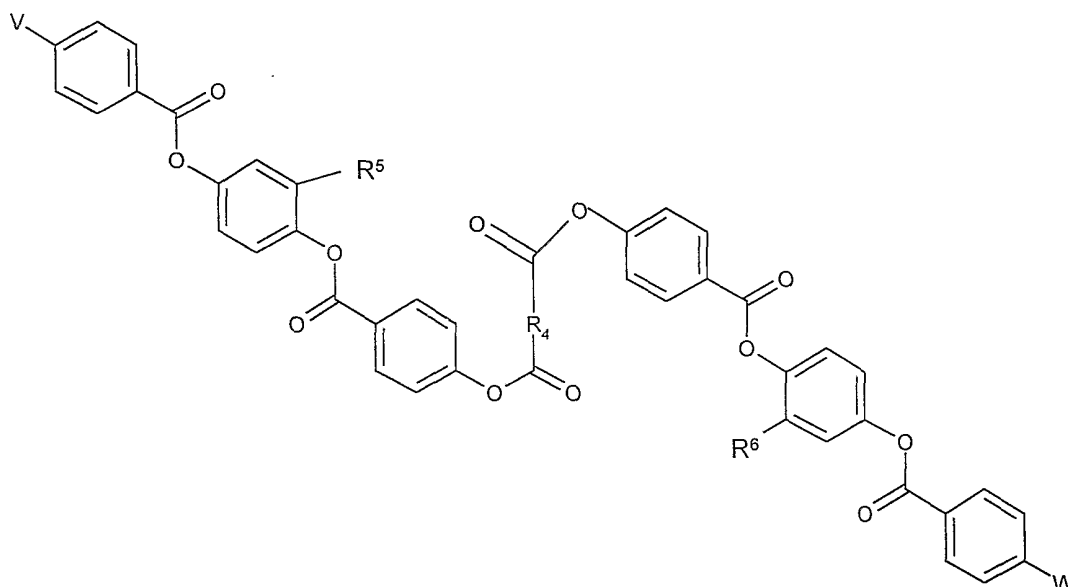
wherein

R^4 has from about 2 to about 20 carbon atoms, preferably from about 2 to
 5 about 12 carbon atoms, and most preferably from about 6 to about 12
 carbon atoms.

the alkyl substituent on the central aromatic group of the aromatic ends
 includes, but is not necessarily limited to t-butyl groups, isopropyl
 groups, and secondary butyl groups. Most preferred are t-butyl groups;
 10 and,

V and W are selected from the group consisting of terminal functionalities and
 polymerizable groups. In platform molecules, V and W are terminal
 functionalities. In polymerizable mesogens, V and/or W are
 polymerizable groups.

15 The same procedures may be used to make mesogens having the following
 general structure:



wherein

R^5 and R^6 are selected from the group consisting of hydrogen, halogen, alkyl groups having from about 1 to 6 carbon atoms, and aryl groups; and,

5 V and W independently are selected from the groups comprising polymerizable groups and terminal functionalities.

Suitable terminal functionalities independently are selected from the group consisting of hydroxyl groups, amino groups, and sulfhydryl groups. Most preferred terminal functionalities are hydroxyl groups.

10 Suitable polymerizable groups may be polymerized by either nucleophilic addition, free radical polymerization, or a combination thereof. Preferred polymerizable groups are polymerizable by Michael addition. Michael addition requires the addition of a nucleophile and an electron deficient alkene. Groups suitable for polymerization by Michael addition include but are not necessarily

15 limited to the examples found in A. Michael, *J. Prakt. Chem.* [2] 35, 349 (1887); R. Connor and W. R. McClelland, *J. Org. Chem.*, 3, 570 (1938); and C. R. Hauser, M. T.

Tetenbaum, *J. Org. Chem.*, **23**, 1146 (1959), all of which are incorporated by reference herein.

Examples of suitable polymerizable groups include, but are not necessarily limited to substituted and unsubstituted alkenyl ester groups comprising a
5 polymerizable unsaturated carbon-carbon bond, wherein said alkenyl group has from about 2 to about 12 carbon atoms, preferably from about 2 to about 9 carbon atoms, more preferably from about 2 to about 6 carbon atoms. Preferred alkenyl esters are acryloyloxy groups and methacryloyloxy groups. V and W may be the same or different, depending upon the application. In a preferred application--a dental
10 application--V and W comprise terminal alkenyl groups.

These alkylendioic bis-(4-{2-alkyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy carbonyl}-phenyl) esters are novel compounds, and may be used as "platform molecules," or polymerizable mesogens. A most preferred alkylendioic bis-(4-{2-alkyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy carbonyl}-phenyl) ester is decanedioic
15 acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy carbonyl}-phenyl) ester.

In order to make the dihydroxyaromatic terminated mesogens, 1,4 bis(4'-hydroxybenzoyloxy) t-butylphenylene or bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy carbonyl}-phenyl) ester is dissolved in a solvent at a ratio of
20 about 10 ml. solvent per gram. The material is dissolved in the solvent under an inert gas, preferably dry nitrogen. Suitable solvents are heterocyclic bases, with a preferred solvent being pyridine. This first mixture is diluted with a chlorinated organic solvent, preferably methylene chloride, in an amount equal to the volume of pyridine.

A second mixture is formed by dissolving an alkyl chloride in a chlorinated

organic solvent at a ratio of about 10 ml solvent per gram of alkyloyl chloride. A preferred chlorinated organic solvent is methylene chloride. The alkyloyl chloride comprises an alkyl portion having from about 2 to about 20 carbon atoms, preferably from about 6 to about 20 carbon atoms, more preferably from about 6 to about 12 carbon atoms, and most preferably is sebacoyl chloride. This second mixture includes at least some of benzoquinone inhibitor, suitable concentrations being from about 1 to about 100 ppm, with a preferred concentration being about 10 ppm. The second mixture is added slowly to the first mixture with stirring, preferably with a syringe through a suba seal. After about 24 hours at room temperature, a precipitate is seen.

10 The solvent, preferably methylene chloride and pyridine, are pumped off.

Any remaining pyridine is converted to a salt using a suitable acid, preferably hydrochloric acid, and the salt is removed by washing with water. Water is filtered off from the remaining white precipitate. Residual water is removed using a suitable solvent, preferably acetone, to dissolve the remaining precipitate, which is then stirred

15 with a suitable amount of magnesium sulfate. The solution is dried down and a dissolved in a chlorinated organic solvent, preferably methylene chloride (DCM), is added to dissolve the solid. After 24 hours at room temperature the unreacted 1,4 bis(4'-hydroxybenoyloxy) t-butylphenylene crystallizes out of solution as a white precipitate and separated from the mixture. The solution was then placed in the

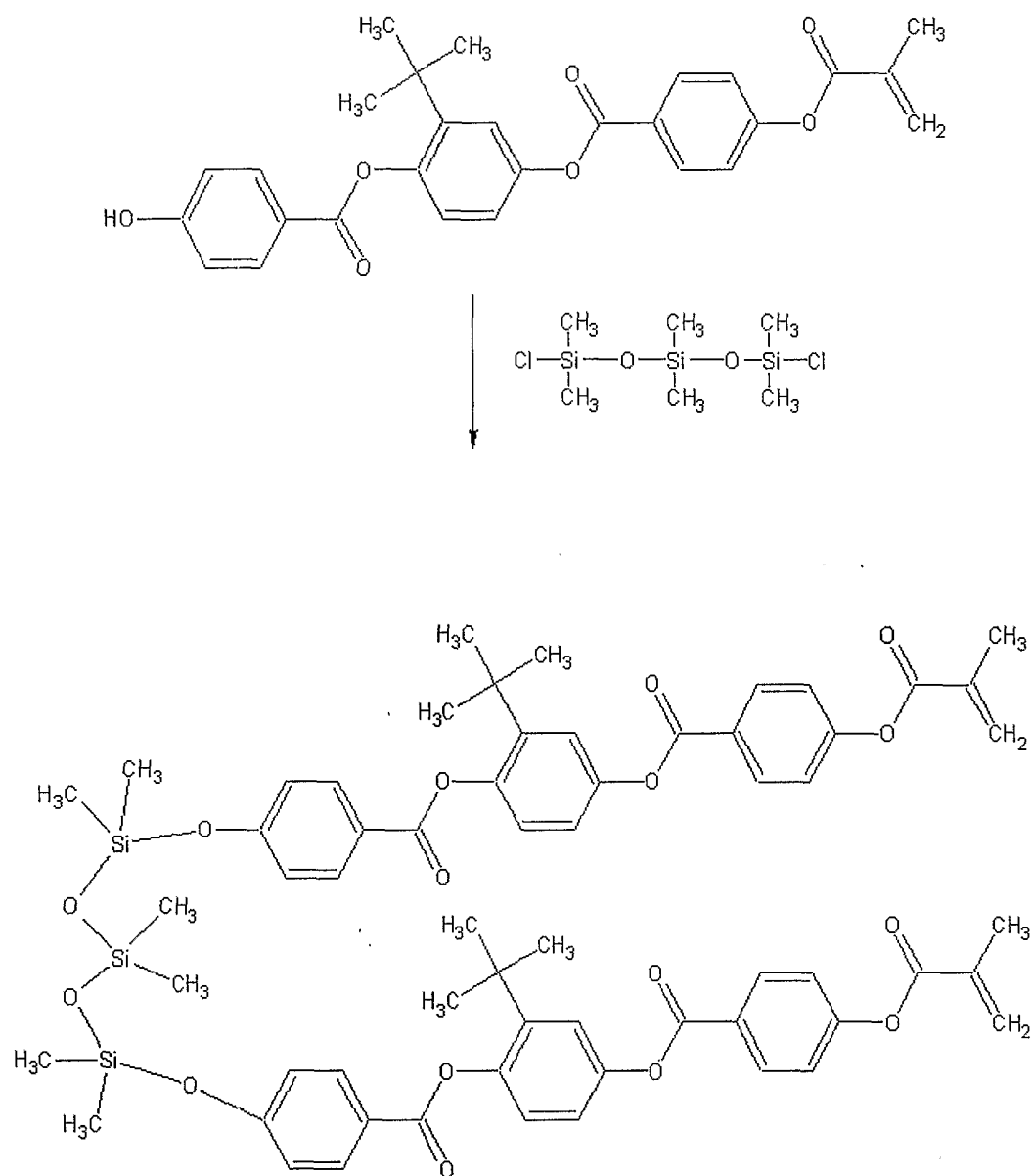
20 freezer overnight and decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester precipitates out of solution. Silica and basic alumina may be added to absorb any remaining methacrylic acid or carboxylic acid terminated products.

Aromatic terminated mesogens (herein called "mesogenic dimers"), such as the

foregoing, are used as a diluent and blended with the aliphatic terminated mesogens (herein called polymerizable mesogen) to form the polymerizable mixture. The quantity of mesogenic dimer in the blend will vary depending upon the dimer and its impact on transition temperature, final product, etc.

5 **-Reaction of dimethyl amine or dichloro terminated
oligodimethylsiloxanes with the mono methacrylate ester of 1,4
[4'-hydroxybenzoyloxy] t-butylphenylene**

 Molecules with high temperature stability can be prepared by reacting dimethyl
10 amine or dichloro terminated oligodimethylsiloxanes with the mono methacrylate
ester of 1,4 [4'-hydroxybenzoyloxy] t-butylphenylene, as shown below:



In this embodiment, the mesogenic platform molecule 1,4 [4'-hydroxybenzoyloxy] t-butylphenylene is further extended by reaction with p-anisoyl chloride and subsequent ether methyl group cleavage with aluminum chloride and ethane thiol. Fully aromatic diphenol terminated mesogens of any length
5 can be thus produced. Reaction with acryloyl or methacryloyl chloride forms the monoester, which can be coupled to reactive aliphatic or siloxane oligomers to form polymerizable liquid crystals with reactive ends.

Formation of alkoxy terminal functionalities

In order to produce alkoxy functionalities, an excess of anisoyl chloride is
10 mixed with a desired 1,4 bis(4'-hydroxybenzoyl oxy)-R² phenylene, (preferably a t-butylphenylene) in an excess of pyridine and triethyl amine (about a 10:1 ratio) with stirring under nitrogen for several hours, preferably about 4hr. The pyridine is removed under vacuum, and the mixture is extracted into ethyl ether. Amine hydrochloride is removed by vacuum filtration and the remaining solids are washed
15 with a suitable solvent, such as water and acetone. The product had a melting point of 222-224 °C and the structure of the molecule was confirmed by NMR to be the aromatic dimethoxy compound.

Low Polymerization Shrinkage

The mesogens exhibit low polymerization shrinkage. Polymerization shrinkage
20 is measured by codissolving the monomers in dichloromethane with 0.3 wt.% camphorquinone photoinitiator, 100 ppm benzoquinone and 1 wt.% N,N'-dimethylaminoethyl methacrylate activator and subsequently pumping off the solvent, all under yellow light. The monomers are then polymerized in film or droplet form in

less than 1 minute by exposure to a dental curing light (Dentsply Spectrum Curing Lamp) with a significant output at 420 nm.

FTIR spectroscopy (Nicolet Magna-IR 560) is used to measure the degree of cure by observing the decrease in the 1637 cm^{-1} alkene band vs. the aromatic internal thickness band at 1603 cm^{-1} . Thin film measurements that avoid oxygen inhibition are performed by sandwiching the monomer between polyvinylidene chloride films, which have an optical window in the wavelength region of interest. The IR spectrum of solid droplets is evaluated using a single bounce reflectance measurement. The flat bottom surface of the droplet is pressed against the germanium lense of a Spectra Tech Thunderdome attachment.

Polymerization of the monomers can be observed between transparent polyvinylidene chloride films under cross-polarized optical microscopy in the heated stage of a Nikon Optimat microscope. Little change in the local birefringence and thus local orientation is noted upon polymerization at room temperature or upon heating to 180°C .

Fracture Toughness

Compact tension samples (ASTM E399) with known edge crack length are fabricated by photocuring monomer with initiator and activator in silicone molds. After polishing the surface with 600 grit polishing agent and soaking in physiologic saline at 37°C for 24 hours the samples are tested at room temperature under displacement control at 1mm/min until failure.

The fracture toughness of the crosslinked, amorphous glass is as high as possible, suitably $0.4\text{ Mpa}\cdot\text{m}^{1/2}$ or higher, preferably $0.5\text{ MPa}\cdot\text{m}^{1/2}$ or higher, which is the same as that found for photocured, isotropic dimethacrylate based

resins such as GTE resin (3M company).

Fillers

Considerable amounts of soluble impurity can be added to the polymerizable mesogens, or a mixture comprising the polymerizable mesogens, without changing the $T_{\text{nematic} \rightarrow \text{isotropic}}$ transition temperature of the polymerizable mesogens. Thus, a high volume fraction of filler can be added to the polymerizable mesogens and still form a composite that maintains desirable, low viscosity flow and low polymerization shrinkage characteristics at temperatures of curing. Commercial products add up to about 70-80 wt% filler. A preferred embodiment uses about 30 wt.% filler.

A variety of fillers may be used. A preferred filler is amphoteric nano-sized metal oxide particles having a diameter in nanometers which is sufficiently small to provide transparency effective for photopolymerization but sufficiently large to provide effective fracture toughness after photopolymerization. Substantially any "metal" capable of forming an amphoteric metal oxide may be used to form the metal oxide particles. Suitable metallic elements include, but are not necessarily limited to niobium, indium, titanium, zinc, zirconium, tin, cerium, hafnium, tantalum, tungsten, and bismuth. Also suitable in place of the metal in the oxide is the semi-metallic compound, silicon. As used herein, unless otherwise indicated, the term "metal oxide" is defined to include silicon, and the word "metal," when used to refer to the metal oxide is intended to also refer to silicon.

The metal oxides may be made of a single metal, or may be a combination of metals, alone or combined with other impurities or "alloying" elements, including, but not necessarily limited to aluminum, phosphorus, gallium, germanium, barium, strontium, yttrium, antimony, and cesium.

A monomeric liquid crystal (LC) containing a high volume fraction of filler nanoparticles is a highly constrained system. As a result, at least for some monomeric species, both smectic and crystalline transitions should be suppressed. The consequent widening of the stability range of nematic mesophase should permit the composite to polymerize at much lower temperatures than in unfilled systems, resulting in lower polymerization shrinkage.

The metal oxide nanoparticles may be prepared using any known methods, such as "sol-gel" techniques, direct hydrolysis of metal alkoxides by water addition, forced hydrolysis of relatively low-cost metal salts, or non-hydrolytic reactions of metal alkoxides with metal halide salts. Examples of such procedures are shown in the following references, each of which is incorporated herein by reference: W. Stöber and A. Fink, *J. of Colloid and Interface Science*, v. 26, 62-69 (1968); M.Z.-C. Hu, M.T. Harris, and C.H. Byers, *J. of Colloid and Interface Science*, v. 198, 87-99 (1988); M. Ocaña and E. Matijević, *J. of Materials Research*, v. 5(5), 1083-1091 (1990); L. Lerot, F. LeGrand, P. de Bruycker, *J. of Materials Science*, v. 26, 2353-2358 (1991); H. Kumazawa, Y. Hori, and E. Sada, *The Chemical Eng'g. Journal*, v. 51, 129-133 (1993); S. K. Saha and P. Pramanik, *J. of Non-Crystalline Solids*, v. 159, 31-37 (1993); M. Andrianainarivelo, R. Corriu, D. Leclercq, P.H. Mutin, and A. Vioux, *J. of Materials Chemistry*, v. 6(10), 1665-1671 (1996); F. Garbassi, L. Balducci, R. Ungarelli, *J. of Non-Crystalline Solids*, v. 223, 190-199 (1998); J. Spatz, S. Mössmer, M. Möllner, M. Kocher, D. Neher, and G. Wegner, *Advanced Materials*, v. 10(6), 473-475 (1998); R. F. de Farias, and C. Airoidi, *J. of Colloid and Interface Science*, v. 220, 255-259 (1999); T. J. Trentler, T. E. Denler, J. F. Bertone, A. Agrawal, and V.L. Colvin, *J. of the Am. Chemical Soc.*, v. 121, 1613-1614 (1999);

Z. Zhan and H.C. Zheng, J. of Non-Crystalline Solids, v. 243, 26-38 (1999); M. Lade, H. Mays, J. Schmidt, R. Willumeit, and R. Schomäcker, Colloids and Surfaces A: Physiochemical and Eng'g Aspects, v. 163, 3-15 (2000); and the procedure described in "Sol-gel processing with inorganic metal salt precursors," authored by "Michael" Zhong Cheng Hu, licensable via Oak Ridge National Laboratory under ORNL control number ERID 0456.

The application will be better understood with reference to the following examples, which are illustrative only:

Example 1

Synthesis of 4-nitrophenylenecarbonyloxy 6'-hexane-1'-ol

60 g 4-nitrobenzoic acid (0.4 mole) was dissolved in 250 ml (2.07 mole) dry hexanediol that had been fused in the reaction vessel at 165 °C. 1 ml. tetrabutyltitanate catalyst was added, and the mixture was stirred for 3 hours at 135 °C before cooling to 95 °C where stirring was continued under dynamic vacuum for two days to remove the water of condensation.

The solution was extracted with 1 liter diethyl ether, centrifuged or filtered to remove the catalyst, and then washed two times with 500 ml 5% NaHCO₃ to remove unreacted acid and excess diol. After the ether was vacuum evaporated, the residue was dissolved in 150 ml boiling ethanol to which 75 ml water was added. Upon cooling to room temperature bis 1,6-(4 nitrophenylene carbonyloxy)hexane precipitated as 7.61 grams of a yellow powder ($T_m = 112\text{ }^{\circ}\text{C}$).

The remaining solution was evaporated and redissolved in 150 ml diethyl ether to which was added 75 ml hexane. After crystallization at -20 °C 4-nitrophenylene 4-

carbonyloxy 6'-hexane-1'-ol (86.7 grams) was isolated ($T_m=32-35\text{ }^{\circ}\text{C}$). NMR indicated that both of these products were greater than 98% purity.

Example 2

Synthesis of 4-(6-hydroxyhexyloxy)phenylenecarbonyloxy 6'-hexane 1'-ol

- 5 20 ml (0.166 mole) of dry, molten hexanediol was transferred to a flask with an attached short path distillation unit. 200 ml dry dimethylsulfoxide (DMSO) and then 40 ml of 1M KOBu^t was then added to the diol and stirred 45 minutes at room temperature. The Bu^tOH and a small amount of DMSO were distilled off under vacuum between 25-50 °C over one hour. 8ml (0.04 mole) of dry 4-
- 10 nitrophenylenecarbonyloxy 6'-hexane-1'-ol was added producing a bright blue color that converted to a yellow coloration after 2 hours.

After stirring overnight, the DMSO and excess hexanediol was removed by vacuum distillation at 90 °C, whereupon the residue was taken up in 200 ml diethyl ether which was washed twice with 200 ml 5% NaHCO₃ and dried with MgSO₄.

- 15 After the ether was distilled away, the solid was dissolved in a minimum amount of boiling ethanol and crystallized at -20°C. A 75-90% yield of the desired white product was obtained ($T_m=30-33^{\circ}\text{C}$).

Example 3

Synthesis of 4-[6-hydroxyhexyloxy] benzoic acid

- 20 1.2 g (0.0037 mole) 4-(6-hydroxyhexyloxy)phenylenecarboxyloxy 6'-hexane 1'-ol was heated for 8 hours at 90 °C in a solution of 0.29 g (0.0074 mole) NaOH in 4 ml water. 20 ml of water was added to the clear solution and 0.3 ml of concentrated HCl added to precipitate the acid at pH=3-5. The white solid was filtered off and dried

under vacuum to produce a quantitative yield of the substituted benzoic acid ($T_m=117^{\circ}\text{C}$).

Example 4

Synthesis of 4 (6'-chlorohexyloxy) benzoyl chloride

5 A three times molar excess of thionyl chloride (55ml) in toluene (300ml) was dropwise added over 20 minutes to 4-(6'-hydroxyhexyloxy)benzoic acid (60g, 0.252 mole) suspended in toluene (600ml) with a stoichiometric amount of pyridine (42 ml) at 0°C . The suspension was continuously stirred for another 8 hours at room temperature, whereupon the toluene and excess thionyl chloride were distilled off at
10 $70-100^{\circ}\text{C}$ with a slight nitrogen flow. The remaining slush of the pyridine hydrochloride and product was extracted with 1l boiling hexane and mixed with 5 g basic alumina and 5g neutral silica and filtered hot. A 90% yield of a very light yellow 4-(6'-chlorohexyloxy)benzoyl chloride liquid was obtained after evaporation of the hexane ($T_m < 20^{\circ}\text{C}$).

15

Example 5

Synthesis of bis 1,4 [4''-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene

65g of 4-(6'-chlorohexyloxy)benzoyl chloride (0.23 mole) was added to 16.75 g (0.1 mole) of t-butyl hydroquinone dissolved in 800 ml dry diethyl ether. 10 ml pyridine and 32 ml triethylamine were then added to this mixture. After stirring for
20 20 hours, the ether was filtered and washed two times with 200 ml 0.1N HCl and 200 ml saturated NaCl solution. The ether solution was then mixed with 10g basic alumina to remove unreacted acid and 10 g neutral silica to flocculate the suspension and dried over magnesium sulfate. The product starts to crystallize from the ether when the solution is reduced by half. After continued crystallization at -20°C

overnight 63 g of product melting at 95-100 °C could be obtained. Another crop of crystals was obtained by further reducing the solution and crystallizing at -20°C over one week. NMR purity was >99%.

Example 6

5 Synthesis of bis 1,4 [4''-(6'-iodohexyloxy)benzoyloxy] t-butylphenylene

1.15 g (0.0016 mole) bis 1,4 [4''-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene dissolved in 20 ml acetone was boiled under nitrogen with 8.0 g NaI in 20 ml acetone for 20 hours. A quantitative yield of bis 1,4 [4''-(6'-iodohexyloxy)benzoyloxy] t-butylphenylene was obtained. The material melted at 76
10 °C and was >99% pure by NMR.

Example 7

Synthesis of bis 1,4 [4''-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene

36 g of bis 1,4 [4''-(6'-chlorohexyloxy)benzoyloxy] t-butylphenylene was dissolved in 750 ml of n-methylpyrrolidinone (NMP) in a single neck flask. 15g KBr
15 and 120 ml water were then added. The flask was then wired shut with a suba seal, and the solution was heated to 120 °C for 24 hours. Upon cooling, the solution was quenched into 1500 ml water and extracted with 250 ml methylene chloride. After evaporation of the methylene chloride, the solid was extracted with 1l of ether and washed with 1l water and dried with MgSO₄. The solution was concentrated and
20 crystallized at -20 °C for 3 days to yield 17 g of white product melting at 80 °C. Additional product crystallized from the solution after several weeks. NMR purity was >99%.

Stopping the above reaction at intermediate times yielded mixtures of di-OH terminated, and asymmetric monochloro, monohydroxy compounds.

Example 8**Synthesis of bis 1,4 [4''-(6'-methacryloyloxyhexyloxy)benzoyloxy] t-butylphenylene**

5 10 g (0.0165 mole) bis 1,4 [4''-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 200 ml dry methylene chloride containing 100 ppm benzoquinone (free radical quencher). After cooling the above solution to 0 °C 3.2 ml (0.035 mole) distilled methacryloyl chloride was then added along with 3 ml (0.037 mole) pyridine and the solution was stirred for 24 hours in a sealed flask making no
10 attempt to remove air from the solvent.

The solvent was vacuum evaporated and the resultant solid taken up in 250 ml ether and washed with 250 ml 0.1N H Cl and 250 ml saturated NaCl. After drying with MgSO₄ and filtering, the solvent was evaporated to yield 10 g of the desired product as a nematic liquid, which was >98% pure by NMR. This material could be
15 crystallized from diethyl ether at -20 °C to form a white crystalline solid melting at 57 °C.

Example 9**Synthesis of bis 1,4 [4''-(6'-cinnamoyloxyhexyloxy)benzoyloxy] t-butylphenylene**

5 g (0.0825 mole) of bis 1,4 [4''-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 100 ml dry methylene chloride containing 100 ppm
20 benzoquinone (free radical quencher). After cooling the above solution to 0 °C, 3.0 g (0.018mole) cinnamoyl chloride was then added along with 1.4 ml (0.017 mole) pyridine, and the solution was stirred for 24 hours in a sealed flask making no attempt to remove air from the solvent.

The solvent was vacuum-evaporated and the resultant solid taken up in 100 ml ether and washed with 100 ml 0.1N HCl and 250 ml saturated NaCl. After drying with MgSO₄ and filtering, the solvent was evaporated to yield 5 g of the desired product which was >98% pure by NMR. This material could be crystallized from diethyl ether at -20 °C to form a white crystalline solid melting at 70 °C.

Example 10

Synthesis of bis 1,4 [4''-(6'-acetoxyoxyhexyloxy)benzoyloxy] t-butylphenylene

1 g (0.0165 mole) of bis 1,4 [4''-(6'-hydroxyhexyloxy)benzoyloxy] t-butylphenylene was dissolved in 20 ml dry methylene chloride. After cooling the above solution to 0 °C, 0.27 ml (0.0037 mole) acetyl chloride was then added along with 0.3 ml pyridine, and the solution was stirred for 24 hours in a sealed flask.

The solvent was vacuum-evaporated and the resultant solid taken up in 20 ml ether and washed with 20 ml 0.1N HCl and 250 ml saturated NaCl. After drying with MgSO₄ and filtering, the solvent was evaporated to yield the product quantitatively at >98% purity by NMR. This material could be crystallized from diethyl ether at -20 °C to form a white crystalline solid melting at 82 °C.

Example 11

Synthesis of 1,4 Bis(4'-methoxybenzoyloxy)t-butylphenylene

Anisoyl chloride (4.93 g, 0.029 mole), t-butyl hydroquinone (2.00 g, 0.012 mole) in pyridine (50 ml) and triethyl amine (3.2 ml) were stirred under nitrogen for 4 hours with the mixture eventually becoming dark orange/red. The pyridine was removed under vacuum and the mixture was precipitated into ethyl ether (500 ml). Amine hydrochloride precipitated out of solution and was removed by vacuum filtration. The ether was evaporated and the slightly yellow crystals were dissolved in

chloroform and extracted with slightly acidified water. The color of the crystals was then removed by stirring over basic alumina and the crystals were then purified by recrystallization in isopropanol. 4.8 grams of material was collected (88% yield) with a melting point of 138-140 °C. The structure of the molecule was confirmed by

5 NMR.

Example 12

Synthesis of 1,4 Bis(4'-hydroxybenzoyloxy) t-butylphenylene

1,4 Bis(4-methoxybenzoyloxy) t-butylphenylene (0.5 g., 0.00115 mole) and aluminum chloride (1.23 g., 0.00921 mole) were added to ethane thiol (2.5 ml) and

10 dichloromethane (2.5 ml) to form a slightly yellow solution. This mixture was stirred for 1 hour and a white solid precipitated out of solution during this time. The mixture was precipitated into 200 ml of water and extracted with ethyl ether. The ether was evaporated and 0.432 grams were recovered, (92% yield). The melting point was not determined, but was found in be in excess of 280 °C.

15

Example 13

Synthesis of 1,4 Bis(4''-(4'-methoxybenzoyloxy)benzoyloxy)t-butylphenylene

The dark orange solution of anisoyl chloride (0.357 g, 2.096 mmole), 1,4 bis(4'-methoxybenzoyloxy) t-butylphenylene (0.355 g, 0.873 mmole) in pyridine (25 ml) and triethyl amine (0.5 ml) were stirred under nitrogen for 4 hr. The pyridine was

20 removed under vacuum, and the mixture was extracted into ethyl ether (200 ml). Amine hydrochloride and the product were insoluble and were removed by vacuum filtration. The amine hydrochloride was removed by washing the solids with water and acetone. The product had a melting point of 222-224 °C and the structure of the molecule was confirmed by NMR.

Example 14**Synthesis of 1,4 Bis(4'-methacryloylbenzoyloxy) t-butylphenylene and 1-(hydroxybenzoyloxy),4-(4'-methacryloylbenzoyloxy) t-butylphenylene**

5 0.2 g (4.92×10^{-4} mole) 1,4 bis(4'-hydroxybenzoyloxy) t-butylphenylene was dissolved in 1 ml pyridine containing 10 ppm benzophenone, and to this was slowly added 0.026 ml (2.46×10^{-4} mole) methacryloyl chloride dissolved in 2 ml methylene chloride. After stirring for 12 hours at room temperature, the methylene chloride was pumped off and the remaining pyridine solution was diluted into 0.1 N

10 HCl to neutralize the pyridine and precipitate the product. After washing the precipitate with water and drying under vacuum, the precipitate was taken up into ether and dried with MgSO_4 . After ether evaporation, the suspension was taken up into 3 ml methylene chloride in which the starting diphenol was insoluble. After filtering away the diphenol, the monomethacrylate ($T_m = 230^\circ\text{C}$) was crystallized

15 from the remaining solution at room temperature by the addition of 3ml hexane. The remaining clear solution contained mainly the dimethacrylate in very small amounts ($T_m = 142^\circ\text{C}$).

Example 15**Synthesis of bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester {C0[H,TB,H] (MeAcry)(O)}₂**

20 In order to make decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester {C0[H,TB,H] (MeAcry)(O)}₂ (seb), 0.95g, 1.95mmole of 1-(hydroxybenzoyloxy),4-(4'-methacryloylbenzoyloxy) t-butylphenylene was dissolved in 10 ml dry pyridine under

25 dry nitrogen and then diluted with 20 ml dry methylene chloride. 0.233g sebacoyl chloride (0.975mmol) was dissolved in 10 ml dry methylene chloride containing

10ppm benzoquinone inhibitor and added slowly with syringe through a suba seal into the first solution with stirring. After 29 hours at room temperature a small amount of precipitate was seen and the methylene chloride was pumped off and 0.01g paradimethylaminopyridine was added as a catalyst to continue the reaction.

5 After another 24 hours at room temperature, some unconverted phenol was still observed by TLC and 0.5ml methacryloyl chloride was dissolved in 10 ml dry methylene chloride and added to the reaction mixture to react any unconverted starting material to the dimethacrylate. After 3 hours the phenol had been completely converted and methylene chloride was removed under vacuum.

10 100ml of water containing 7.5ml concentrated HCl was added to the flask with stirring and stirred for four hours to remove the pyridine as the hydrochloride salt (pH=4). The water layer could be poured from the white layer which stuck to the walls of the vessel. After washing once more with deionized water, 100ml methylene chloride was added to dissolve the solid and the resulting organic phase was
15 transferred to a separatory funnel and washed twice with 100ml brine saturated water and dried with magnesium sulfate. One gram each of silica and basic alumina were added to absorb any remaining methacrylic acid or carboxylic acid terminated products.

 After standing for 8 hours the methylene chloride solution was filtered and
20 added to 500ml of stirred hexane. After 8 hours the pure precipitated product was collected; the supernatant contained methacrylated starting material.

 The white precipitate eluted in 80/20 ether/hexane on silica as a major spot and a very faint following spot. NMR revealed about 95% purity of the desired product (30% yield) with the rest being a methoxy terminated product which was carried over

from the diphenol starting material. Solutions could be cast into a translucent, nematic glass at room temperature which gradually softened upon heating.

Example 16

5 **Synthesis of Decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester**

18.25g, (44.9mmole) of 1,4 bis(4'-hydroxybenzoyloxy) t-butylphenylene was dissolved in 120 ml dry pyridine under dry nitrogen and then diluted with 100 ml dry methylene chloride. 1.34g sebacyl chloride (5.60mmol) was dissolved in 20 ml dry methylene chloride and added slowly with syringe through a suba seal into the first solution with stirring. After 24 hours at room temperature a small amount of precipitate was seen and the methylene chloride and pyridine were pumped off

300ml of water containing 7.5ml concentrated HCl was added to the flask with stirring and stirred for four hours to remove the pyridine as the hydrochloride salt (pH=4). The water was filtered off from the white precipitate that formed in the vessel. 200ml of acetone was added to dissolve the mixture which was then stirred with 3 grams of magnesium sulfate to remove any remaining water, after which the solution was dried down. 200ml methylene chloride (DCM) was added to dissolve the solid. After 24 hours at room temperature the unreacted 1,4 bis(4'-hydroxybenoyloxy) t-butylphenylene crystallized out of solution as a white precipitate. The solution was then placed in the freezer overnight and decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester precipitated out of solution.

25 The white precipitate eluted in 90/10 DCM/acetone on silica as a major spot and a very faint spots resulting from higher order polymerization. The product had a high

NMR purity (>95%)..

Example 17

5 **Synthesis of Decanedioic acid bis-(4-{2-tert-butyl-4-[4-(2-methyl-acryloyloxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester**

0.85g, (0.868mmole) of decanedioic acid bis-(4-{2-tert-butyl-4-[4-(hydroxy)-benzoyloxy]-phenoxy-carbonyl}-phenyl) ester was dissolved in 20ml dry pyridine under dry nitrogen and then diluted with 20ml dry methylene chloride. 0.118g methacryloyl chloride (1.13mmol) was dissolved in 10 ml dry methylene chloride containing 10ppm benzoquinone inhibitor and added slowly with syringe through a suba seal into the first solution with stirring. After 24 hours at room temperature a small amount of precipitate was seen and the methylene chloride and pyridine were pumped off.

100ml of water containing 1.0ml concentrated HCl was added to the flask with stirring and stirred for two hours to remove the pyridine as the hydrochloride salt (pH=4). The water layer could be poured from the white layer, which stuck to the walls of the vessel. After washing once more with deionized water. 50ml methylene chloride was added to dissolve the solid and the resulting organic phase was transferred to a separatory funnel and washed twice with 100ml brine saturated water and dried with magnesium sulfate. One gram each of silica and basic alumina were added to absorb any remaining methacrylic acid or carboxylic acid terminated products. NMR revealed that the product was the desired dialkene terminated monomer.

Example 18.**Bis 1,4 [4-hydroxybenzoyloxy] 2-phenyl-phenylene**

(100 g, 0.537 mole) of phenylhydroquinone and (229 g, 1.342 mole) of anisoyl chloride were added to 100 ml of pyridine and 500 ml of dry dichloromethane. The mixture was stirred for 72 hours at room temperature under nitrogen gas until it was mostly solidified. The 1,4 bis [4-methoxybenzoyl 2-phenyl phenylene] was recrystallized from isopropyl alcohol for a 96% yield.

(42.72 g, 0.094 mole) of the 1,4 bis [4-methoxybenzoyl] 2-phenyl phenylene was added to a solution consisting of (100 g, 0.749 mole) of aluminum chloride, (58.21 g, 0.937 mole) of ethane thiol and (199.04 g, 2.344 mole) of dichloromethane. After one hour the reaction was quenched with 250 ml of isopropyl alcohol. The solids were filtered and the product 1,4 bis [4-hydroxybenzoyl] 2-phenyl phenylene was purified by extraction of the solid material with water and dichloromethane for a 68.6% yield. It is suspected that the isopropyl alcohol partially solubilizes the product and yield was lost in the filtration of the precipitated material. NMR was used to confirm the structure and purity of the material.

Example 19.**Bis 1,4 [4-hydroxybenzoyloxy] 2-methyl phenylene**

(29g, 0.23 mole) of methylhydroquinone and (100 g, 0.58 mole) of anisoyl chloride were added to 50 ml of pyridine and 250 ml of dry dichloromethane. The mixture was stirred for 72 hours at room temperature under nitrogen gas until it was mostly solidified. The 1,4 bis [4-methoxybenzoyl] 2-methyl phenylene was recrystallized from isopropyl alcohol for a 95% yield. (m.p. 172-174°C)

(90 g, 0.229 mole) of the 1,4 bis [4-methoxybenzoyl 2-methyl phenylene] was added to a solution consisting of (250 g, 1.835 mole) of aluminum chloride, (142.27

g, 2.290 mole) of ethane thiol and (486 g, 5.725 mole) of dichloromethane. After one hour the reaction was quenched with 880 ml of isopropyl alcohol. The solids were filtered and the product 1,4 bis [4-hydroxybenzoyl}2-methyl phenylene]was purified by extraction of the solid material with water and dichloromethane for an 84% yield.

5 NMR was used to confirm the structure and purity of the material.

Persons of ordinary skill in the art will recognize that many modifications may be made to the present invention without departing from the spirit and scope of the present invention. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following

10 claims.

I Claim:

- 1 1. A method for producing platform molecules comprising:
2 providing a first phenylene ring comprising a first functional group at a para-
3 position to a second functional group;
4 providing a second phenylene ring comprising a third functional group at a
5 para- position to a fourth functional group;
6 providing a third phenylene ring comprising a desired substituent and
7 comprising a first functionality at a para- position to a second
8 functionality; and
9 reacting said first functional group with said first functionality, producing at
10 least a first ester bond between said first phenylene ring and said third
11 phenylene ring; and
12 reacting said third functional group with said third functionality, producing at
13 least a second ester bond between said second phenylene ring and said
14 third phenylene ring, thereby producing platform molecules
15 comprising a first terminal functionality at position para- to said first
16 intervening ester bond and a second terminal functionality at a position
17 para- to said second intervening ester bond, wherein at least one
18 functionality selected from the group consisting of said first terminal
19 functionality and said second terminal functionality is other than a
20 polymerizable group;
21 wherein, when both said first terminal functionality and said second
22 functionality are polymerizable groups, said desired substituent
23 provides sufficient steric hindrance to achieve a nematic state at room

24 temperature while suppressing crystallinity at room temperature.

1 2. The method of claim 1 wherein both said first terminal functionality
2 and said second terminal functionality are other than polymerizable groups.

1 3. A method for producing platform molecules comprising:
2 providing a first phenylene ring comprising a first functional group at a para-
3 position to a second functional group;
4 providing a second phenylene ring comprising third functional group at a para-
5 position to a fourth functional group;
6 providing a third phenylene ring comprising a desired substituent and
7 comprising a first hydroxyl group at a para- position to a second
8 hydroxyl group; and
9 reacting said first hydroxyl group with said first functional group, producing at
10 least a first ester bond between said first phenylene ring and said third
11 phenylene ring; and
12 reacting said second hydroxyl group with said third functional group,
13 producing at least a second ester bond between said second phenylene
14 ring and said third phenylene ring, thereby producing platform
15 molecules comprising a first terminal functionality at position para- to
16 said first ester bond and a second terminal functionality at a position
17 para- to said second ester bond, wherein at least one functionality
18 selected from the group consisting of said first terminal functionality
19 and said second terminal functionality is other than a polymerizable
20 group;

21 wherein, if one of said first terminal functionality or said second terminal

22 functionality is a polymerizable group;
23 wherein, if both said first terminal functionality and said second functionality
24 are polymerizable groups, said desired substituent provides sufficient
25 steric hindrance to achieve a nematic state at room temperature while
26 suppressing crystallinity at room temperature.

1 4. The method of claim 3 wherein both said first terminal functionality
2 and said second terminal functionality are other than polymerizable groups.

1 5. The method of claim 1 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 6. The method of claim 2 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 7. The method of claim 3 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 8. The method of claim 4 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 9. The method of claim 1 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

1 10. The method of claim 1 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to about 4 carbon
3 atoms and phenyl groups.

1 11. The method of claim 1 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 12. The method of claim 2 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

1 13. The method of claim 2 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to about 4 carbon
3 atoms and phenyl groups.

1 14. The method of claim 2 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 15. The method of claim 3 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

1 16. The method of claim 3 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to about 4 carbon
3 atoms and phenyl groups.

1 17. The method of claim 3 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 18. The method of claim 1 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 19. The method of claim 2 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 20. The method of claim 3 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 21. The method of claim 4 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 22. The method of claim 7 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 23. The method of claim 16 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 24. The method of claim 17 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 25. The method of claim 18 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 26. The method of claim 1 further comprising
2 forming a mixture comprising said platform molecules and at least a fourth
3 phenylene ring comprising a fifth functional group at a position para-
4 to a sixth functional group; and
5 exposing said mixture to conditions effective to form at least a third ester bond
6 between said fourth phenylene ring and a ring selected from the group

7 consisting of said first phenylene ring and said second phenylene ring,
8 thereby producing elongated platform molecules comprising at least
9 four phenylene rings and comprising a new terminal functionality at a
10 position para- to said third ester bond.

1 27. A method for producing polymerizable mesogens comprising:
2 forming a mixture comprising
3 first phenylene rings comprising a first functional group at a position
4 para-to a second functional group;
5 second phenylene rings comprising a third functional group at a
6 position para- to a fourth functional group; and
7 third phenylene rings comprising a desired substituent and comprising
8 a first functionality at a position para- to a second functionality;
9 and
10 exposing said mixture to conditions effective to react said first functional
11 group and said first functionality, forming a first ester bond between
12 said first phenylene ring and said third phenylene ring, and to react
13 said second functional group and said third functionality forming a
14 second ester bond between said second phenylene ring and said third
15 phenylene ring, thereby producing platform mesogens comprising a
16 first terminal functionality at a position para- to said first ester bond
17 and a second terminal functionality at a position para- to said second
18 ester bond, wherein at least one functionality selected from the group
19 consisting of said first terminal functionality and said second terminal
20 functionality is other than a polymerizable group ; and

21 reacting at least one of said first and second terminal functionalities with a
22 polymerizable group, producing polymerizable mesogens;
23 wherein, when both said first terminal functionality and said second
24 functionality are polymerizable groups, said desired substituent
25 provides sufficient steric hindrance to achieve a nematic state at room
26 temperature while suppressing crystallinity at room temperature.

1 28. A method for producing polymerizable mesogens comprising:
2 forming a mixture comprising
3 first phenylene rings comprising a first functional group at a position
4 para- to a second functional group;
5 second phenylene rings comprising a third functional group at a
6 position para- to a fourth functional group; and
7 third phenylene rings comprising a desired substituent and comprising
8 a first hydroxyl group at a position para- to a second hydroxyl
9 group; and
10 exposing said mixture to conditions effective to react said first hydroxyl group
11 and said first functional group, forming a first ester bond between said
12 first phenylene ring and said third phenylene ring, and to react said
13 second hydroxyl group and said third functional group forming a
14 second ester bond between said second phenylene ring and said third
15 phenylene ring, producing platform mesogens comprising a first
16 terminal functionality at a position para- to said first intervening ester
17 bond and a second terminal functionality at a position para- to said
18 second ester bond, wherein at least one functionality selected from the

19 group consisting of said first terminal functionality and said second
20 terminal functionality is other than a polymerizable group; and
21 reacting at least one of said first and second terminal functionalities with a
22 polymerizable group, producing polymerizable mesogens;
23 wherein, when both said first terminal functionality and said second
24 functionality are polymerizable groups, said desired substituent
25 provides sufficient steric hindrance to achieve a nematic state at room
26 temperature while suppressing crystallinity at room temperature.

1 29. The method of claim 27 wherein both said first terminal functionality
2 and said second functionality are other than polymerizable groups.

1 30. The method of claim 28 wherein both said first terminal functionality
2 and said second functionality are other than polymerizable groups.

1 31. The method of claim 27 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 32. The method of claim 28 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 33. The method of claim 29 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 34. The method of claim 30 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 35. The method of claim 27 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

4 36. The method of claim 27 wherein said desired substituent is selected

5 from the group consisting of alkyl groups having from about 1 to about 4 carbon
6 atoms and phenyl groups.

1 37. The method of claim 27 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 38. The method of claim 28 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

1 39. The method of claim 28 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to about 4 carbon
3 atoms and phenyl groups.

1 40. The method of claim 28 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 41. The method of claim 29 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

1 42. The method of claim 29 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to about 4 carbon
3 atoms and phenyl groups.

1 43. The method of claim 29 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 44. The method of claim 30 wherein said desired substituent is selected

2 from the group consisting of alkyl groups having from about 1 to 6 carbon atoms and
3 aryl groups.

1 45. The method of claim 30 wherein said desired substituent is selected
2 from the group consisting of alkyl groups having from about 1 to about 4 carbon
3 atoms and phenyl groups.

1 46. The method of claim 30 wherein said desired substituent is selected
2 from the group consisting of methyl groups, t-butyl groups, isopropyl groups,
3 secondary butyl groups, and phenyl groups.

1 47. The method of claim 27 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 48. The method of claim 28 wherein said second functional group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 49. The method of claim 29 wherein said second reactive group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 50. The method of claim 30 wherein said second reactive group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 51. The method of claim 31 wherein said second reactive group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 52. The method of claim 32 wherein said second reactive group and said

2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 53. The method of claim 35 wherein said second reactive group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 54. The method of claim 40 wherein said second reactive group and said
2 fourth functional group are selected from the group consisting of carboxyl groups and
3 reactive derivatives of carboxyl groups.

1 55. The method of claim 27 further comprising:
2 forming a mixture comprising said platform molecules and at least fourth
3 phenylene rings comprising a fifth functional group at a para- position
4 to a sixth functional group; and
5 exposing said mixture to conditions effective to form at least a third ester bond
6 between said fourth phenylene ring and a ring selected from the group
7 consisting of said first phenylene ring and said second phenylene ring,
8 thereby producing elongated platform molecules comprising at least
9 four phenylene rings and comprising a new terminal functionality at a
10 position para- to said third ester bond.

1 56. The method of claim 27 wherein said polymerizable group comprises
2 a polymerizable unsaturated carbon-carbon bond.

1 57. The method of claim 27 further comprising
2 reacting a first terminal functionality of a first platform molecule with a first
3 end of a bridging agent selected from the group consisting of an α,ω -
4 carboxylic acid and an oligodialkylsiloxane comprising an alkyl group

5 having from about 4 to about 12 carbon atoms; and
6 reacting a first terminal functionality of a second platform molecule with a
7 second, opposed end of said bridging agent.

1 58. A method comprising:
2 providing hydroquinone comprising a desired substituent and comprising a
3 first hydroxyl group at a para- position to a second hydroxyl group;
4 exposing said hydroquinone to 1-(4-chloroalkyloxy) benzoyl chloride under
5 conditions effective to form a first ester linkage between said first
6 hydroxyl group and a first benzoyl group of a first 1-(4-
7 chloroalkyloxy) benzoyl chloride molecule and to form a second ester
8 linkage between said second hydroxyl group and a second benzoyl
9 group of a second 1-(4-chloroalkyloxy) benzoyl chloride molecule,
10 thereby forming a bis-chloro compound comprising bis chlorogroups
11 and a central phenylene ring bearing said desired substituent;

1 wherein, when said bis-chloro groups are converted to polymerizable groups,
2 said desired substituent provides sufficient steric hindrance to achieve
3 a nematic state at room temperature while suppressing crystallinity at
4 room temperature.

1 59. The method of claim 58 wherein said desired substituent is selected
2 from the group consisting of a methyl group and a t-butyl group.

1 60. The method of claim 58, wherein said 1-(4-chloroalkyloxy) benzoyl
2 chloride is produced by:

3 forming a mixture comprising α , ω -substituted alkane comprising an α -
4 hydroxyl group at a first end and an ω - hydroxyl group at an opposed

5 end, and 4-nitrobenzoic acid comprising a nitro- group and a carboxyl
6 group at a position para- to said nitro- group;
7 exposing said mixture to conditions effective to form an ester linkage between
8 said carboxyl group and an entity selected from the group consisting of
9 said α - hydroxyl group and said ω - hydroxyl group, producing 4-(1-
10 hydroxyalkyloxy)benzoic acid(1-hydroxyalkylester) and dimers
11 thereof; and
12 hydrolyzing said dimers, producing 4-(1-hydroxyalkyloxy benzoic acid)
13 comprising 1-hydroxy and a benzoic acid hydroxy moiety;
14 exposing said 4-(1-hydroxyaklyloxy)benzoic acid to a source of chlorine
15 atoms effective to replace said 1-hydroxy and said benzoic acid
16 hydroxy moiety, thereby producing said 1-(4-chloroalkyloxy) benzoyl
17 chloride.

1 61. The method of claim 58 further comprising hydrolyzing said chlorine
2 atoms from said bis chloro compound to produce platform molecules comprising at
3 least one hydroxyalkyloxy terminal functionality.

1 62. The method of claim 59 further comprising hydrolyzing said chlorine
2 atoms from said bis chloro compound to produce platform molecules comprising at
3 least one hydroxyalkyloxy terminal functionality.

1 63. The method of claim 60 further comprising hydrolyzing said chlorine
2 atoms from said bis chloro compound to produce a platform molecules comprising at
3 least one hydroxyalkyloxy terminal functionality.

1 64. The method of claim 61 further comprising collecting said platform
2 molecules.

1 65. The method of claim 62 further comprising collecting said platform
2 molecules.

1 66. The method of claim 63 further comprising collecting said platform
2 molecules.

1 67. The method of claim 61 further comprising reacting said
2 hydroxyalkyloxy terminal functionality with a polymerizable group.

1 68. The method of claim 62 further comprising reacting said
2 hydroxyalkyloxy terminal functionality with a polymerizable group.

1 69. The method of claim 63 further comprising reacting said
2 hydroxyalkyloxy terminal functionality with a polymerizable group.

1 70. The method of claim 64 further comprising reacting said
2 hydroxyalkyloxy terminal functionality with a polymerizable group.

1 71. The method of claim 65 further comprising reacting said
2 hydroxyalkyloxy terminal functionality with a polymerizable group.

1 72. The method of claim 66 further comprising reacting said
2 hydroxyalkyloxy terminal functionality with a polymerizable group.

1 73. The method of claim 61 further comprising
2 reacting a first hydroxyalkyloxy end group on a first platform molecule with
3 an α - end of a bridging agent comprising an α,ω -carboxylic acid; and
4 reacting a second hydroxyalkyloxy end group on a second platform molecule
5 with a ω - end of said bridging agent.

1 74. The method of claim 62 further comprising
2 reacting a first hydroxyalkyloxy end group on a first platform molecule with
3 an α - end of a bridging agent comprising an α,ω -carboxylic acid; and

4 reacting a second hydroxyalkyloxy end group on a second platform molecule
5 with a ω - end of said bridging agent.

1 75. The method of claim 63 further comprising
2 reacting a first hydroxyalkyloxy end group on a first platform molecule with
3 an α - end of a bridging agent comprising an α,ω -carboxylic acid; and
4 reacting a second hydroxyalkyloxy end group on a second platform molecule
5 with a ω - end of said bridging agent.

1 76. The method of claim 64 further comprising
2 reacting a first hydroxyalkyloxy end group on a first platform molecule with
3 an α - end of a bridging agent comprising an α,ω -carboxylic acid; and
4 reacting a second hydroxyalkyloxy end group on a second platform molecule
5 with a ω - end of said bridging agent.

1 77. The method of claim 1 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;
5 and
6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 78. The method of claim 2 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;

5 and
6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 79. The method of claim 3 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;
5 and

6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 80. The method of claim 4 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;
5 and

6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 81. The method of claim 5 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;

5 and
6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 82. The method of claim 8 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;
5 and

6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 83. The method of claim 8 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;
5 and

6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 84. The method of claim 9 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;

5 and
6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 85. The method of claim 15 further comprising
2 reacting a moiety selected from the group consisting of a first hydroxyl group
3 and a first hydroxyalkyloxy end group on a first platform molecule
4 with an α - end of a bridging agent comprising an α,ω -carboxylic acid;
5 and

6 reacting a moiety selected from the group consisting of a second hydroxyl
7 moiety and a second hydroxyalkyloxy end group on a second platform
8 molecule with a ω - end of said bridging agent.

1 86. The method of claim 17 further comprising
2 reacting said first terminal functionality on a first platform molecule with a
3 first end of a bridging agent comprising an oligodialkylsiloxane
4 comprising an alkyl group having from about 4 to about 12 carbon
5 atoms; and,

6 reacting said first terminal functionality on a second platform molecule with a
7 second, opposed end of said bridging agent.

1 87. A method for making platform molecules comprising reacting 4-
2 alkoxy benzoyl chloride with a hydroquinone comprising a desired substituent (R^2)
3 under first conditions effective to produce bis 1,4 [4-alkoxybenzoyloxy]- R^2 -
4 phenylene comprising bis terminal alkoxy groups wherein, when both bis terminal
5 alkoxy groups are converted to polymerizable groups, R^2 provides sufficient steric

6 hindrance to achieve a nematic state at room temperature while suppressing
7 crystallinity at room temperature.

1 88. The method of claim 87 wherein said 4-alkoxy benzoyl chloride is 4-
2 methoxy benzoyl chloride.

1 89. The method of claim 87 wherein said 1,4 [4-alkoxybenzoyloxy-R²-
2 phenylene is subjected to second conditions effective to cleave said bis terminal
3 alkoxy groups, thereby producing a solution comprising diphenolic platform
4 molecules comprising bis terminal hydroxyl groups.

1 90. The method of claim 88 wherein said 1,4 [4-alkoxybenzoyloxy-R²-
2 phenylene is subjected to second conditions effective to cleave said bis terminal
3 alkoxy groups, thereby producing a solution comprising diphenolic platform
4 molecules comprising bis terminal hydroxyl groups.

1 91. The method of claim 87 wherein said first conditions comprise a
2 solution comprising a hydrogen chloride scavenging agent.

1 92. The method of claim 91 wherein said solution further comprises a
2 trialkylamine.

1 93. The method of claim 88 wherein said first conditions comprise a
2 solution comprising a hydrogen chloride scavenging agent.

1 94. The method of claim 93 wherein said solution further comprises a
2 trialkylamine.

1 95. The method of claim 89 wherein said first conditions comprise a
2 solution comprising a hydrogen chloride scavenging agent.

1 96. The method of claim 95 wherein said solution further comprises a
2 trialkylamine.

1 97. The method of claim 90 wherein said first conditions comprise a
2 solution comprising a hydrogen chloride scavenging agent.

1 98. The method of claim 97 wherein said solution further comprises a
2 trialkylamine.

1 99. The method of claim 87 wherein R^2 is selected from the group
2 consisting of methyl groups and t-butyl groups.

1 100. The method of claim 87 wherein
2 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene comprising bis terminal
3 alkoxy groups is to be incorporated into a monomer, R^2 is selected from
4 the group consisting of t-butyl groups, isopropyl groups, secondary butyl
5 groups, methyl groups, and phenyl groups; and,
6 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene is to be incorporated
7 into a dimer, R^2 is selected from the group consisting of bulky organic
8 groups and groups having a bulk less than methyl groups.

1 101. The method of claim 88 wherein R^2 is selected from the group
2 consisting of methyl groups and t-butyl groups.

1 102. The method of claim 88 wherein
2 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene comprising bis terminal
3 alkoxy groups is to be incorporated into a monomer, R^2 is selected from
4 the group consisting of t-butyl groups, isopropyl groups, secondary butyl
5 groups, methyl groups, and phenyl groups; and,
6 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene is to be incorporated
7 into a dimer, R^2 is selected from the group consisting of bulky organic
8 groups and groups having a bulk less than methyl groups.

1 103. The method of claim 89 wherein R^2 is selected from the group
2 consisting of a methyl group and a t-butyl group.

1 104. The method of claim 89 wherein
2 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene comprising bis terminal
3 alkoxy groups is to be incorporated into a monomer, R^2 is selected from
4 the group consisting of t-butyl groups, isopropyl groups, secondary butyl
5 groups, methyl groups, and phenyl groups; and,
6 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene is to be incorporated
7 into a dimer, R^2 is selected from the group consisting of bulky organic
8 groups and groups having a bulk less than methyl groups.

1 105. The method of claim 90 wherein R^2 is selected from the group
2 consisting of a methyl group and a t-butyl group.

1 106. The method of claim 90 wherein
2 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene comprising bis terminal
3 alkoxy groups is to be incorporated into a monomer, R^2 is selected from
4 the group consisting of t-butyl groups, isopropyl groups, secondary butyl
5 groups, methyl groups, and phenyl groups; and,
6 when said bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene is to be incorporated
7 into a dimer, R^2 is selected from the group consisting of bulky organic
8 groups and groups having a bulk less than methyl groups.

1 107. The method of claim 90 wherein said second conditions comprise
2 exposing said bis terminal alkoxy groups to a mixture comprising a quantity of alkyl
3 ether having from about 1 to about 8 carbon atoms and an amount of an aliphatic thiol
4 effective to dissolve a concentration of aluminum chloride in a chlorinated solvent,

5 said exposing taking place at a temperature and for a time effective to selectively
6 cleave said bis terminal alkoxy groups to produce complexes comprising said
7 diphenolic platform molecules comprising intact aromatic ester bonds and to cause
8 said complexes to precipitate out of said solution substantially as they are formed.

1 108. The method of claim 107 wherein said alkyl ethers have from about 1 to
2 about 4 carbon atoms.

1 109. The method of claim 107 wherein said alkyl ether is methyl ether.

1 110. The method of claim 107 wherein said aliphatic thiol comprises an alkyl
2 group having from about 1 to about 11 carbon atoms.

1 111. The method of claim 108 wherein said aliphatic thiol comprises an alkyl
2 group having from about 1 to about 11 carbon atoms.

1 112. The method of claim 109 wherein said aliphatic thiol comprises an alkyl
2 group having from about 1 to about 11 carbon atoms.

1 113. The method of claim 107 wherein said aliphatic thiol is ethane thiol.

1 114. The method of claim 108 wherein said aliphatic thiol is ethane thiol.

1 115. The method of claim 109 wherein said aliphatic thiol is ethane thiol.

1 116. The method of claim 107 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least one mole of thiol per mole of
3 alkyl ether.

1 117. The method of claim 108 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least one mole of thiol per mole of
3 alkyl ether.

1 118. The method of claim 109 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least one mole of thiol per mole of
3 alkyl ether.

1 119. The method of claim 113 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least one mole of thiol per mole of
3 alkyl ether.

1 120. The method of claim 116 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least one mole of thiol per mole of
3 alkyl ether.

1 121. The method of claim 108 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least two moles of thiol per mole of
3 alkyl ether.

1 122. The method of claim 109 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least two moles of thiol per mole of
3 alkyl ether.

1 123. The method of claim 110 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least two moles of thiol per mole of
3 alkyl ether.

1 124. The method of claim 113 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least two moles of thiol per mole of
3 alkyl ether.

1 125. The method of claim 116 wherein said quantity of alkyl ether and said
2 amount of aliphatic thiol is effective to produce at least two moles of thiol per mole of
3 alkyl ether.

1 126. The method of claim 107 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 127. The method of claim 108 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 128. The method of claim 109 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 129. The method of claim 110 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 130. The method of claim 113 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 131. The method of claim 116 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 132. The method of claim 121 wherein said concentration of aluminum
2 chloride produces a ratio of said aluminum chloride to said alkyl ether of 4:1 or more.

1 133. A method for making platform molecules comprising:
2 reacting 4-alkoxy benzoyl chloride with a hydroquinone comprising a desired
3 substituent (R^2) under first conditions comprising a solution
4 comprising a hydrogen chloride scavenging agent effective to produce
5 bis 1,4 [4-alkoxybenzoyloxy]- R^2 -phenylene comprising bis terminal
6 alkoxy groups;

7 wherein, when both of said bis terminal alkoxy groups are converted to
8 polymerizable groups, R^2 provides sufficient steric hindrance to
9 achieve a nematic state at room temperature while suppressing
10 crystallinity at room temperature;

11 subjecting said 1,4 [4-alkoxybenzoyloxy]-R²-phenylene to second conditions
12 effective to cleave said bis terminal alkoxy groups, thereby producing
13 a solution comprising diphenolic platform molecules comprising bis
14 terminal hydroxyl groups, said second conditions comprising an
15 amount of chlorinated solvent comprising at least one mole of thiol per
16 mole of methyl ether and comprising a concentration of aluminum
17 chloride at a molar ratio of 4:1 or more to said methyl ether, said
18 exposing occurring at a temperature and for a time effective to
19 selectively cleave said bis terminal alkoxy groups to produce
20 complexes comprising said diphenolic platform molecules comprising
21 intact aromatic ester bonds and to cause said complexes to precipitate
22 out of said solution substantially as they are formed, said chlorinated
23 solvent being present in an amount effective to maintain said
24 precipitate in slurry form.

1 134. The method of claim 133 further comprising quenching said
2 precipitate.

1 135. The method of claim 133 wherein said amount of chlorinated solvent
2 comprises a molar excess of from about 3 to about 7 relative to said ethane thiol.

1 136. The method of claim 133 wherein said amount of chlorinated solvent
2 comprises a molar excess of 5 or more relative to said ethane thiol.

1 137. The method of claim 134 wherein said amount of chlorinated solvent
2 comprises a molar excess of from about 3 to about 7 relative to said ethane thiol.

1 138. The method of claim 134 wherein said amount of chlorinated solvent
2 comprises a molar excess of 5 or more relative to said ethane thiol.

1 139. The method of claim 133 wherein said temperature comprises an initial
2 temperature of about 0 °C.

1 140. The method of claim 134 wherein said temperature comprises an initial
2 temperature of about 0 °C.

1 141. The method of claim 135 wherein said temperature comprises an initial
2 temperature of about 0 °C.

1 142. The method of claim 136 wherein said temperature comprises an initial
2 temperature of about 0 °C.

1 143. The method of claim 137 wherein said temperature comprises an initial
2 temperature of about 0 °C.

1 144. The method of claim 138 wherein said temperature comprises an initial
2 temperature of about 0 °C.

1 145. The method of claim 133 wherein said chlorinated solvent is
2 methylene chloride.

1 146. The method of claim 134 wherein said chlorinated solvent is
2 methylene chloride.

1 147. The method of claim 138 wherein said chlorinated solvent is
2 methylene chloride.

1 148. The method of claim 144 wherein said chlorinated solvent is
2 methylene chloride.

1 149. The method of claim 133 wherein R² is selected from the group
2 consisting of methyl groups and t-butyl groups.

1 150. The method of claim 133 wherein

2 when said bis 1,4 [4-alkoxybenzoyloxy]-R²-phenylene comprising bis terminal
3 alkoxy groups is to be incorporated into a monomer, R² is selected from
4 the group consisting of t-butyl groups, isopropyl groups, secondary butyl
5 groups, methyl groups, and phenyl groups; and,
6 when said bis 1,4 [4-alkoxybenzoyloxy]-R²-phenylene is to be incorporated
7 into a dimer, R² is selected from the group consisting of bulky organic
8 groups and groups having a bulk less than methyl groups.

1 151. The method of claim 134 wherein R² is selected from the group
2 consisting of methyl groups and t-butyl groups.

1 152. The method of claim 134 wherein
2 when said bis 1,4 [4-alkoxybenzoyloxy]-R²-phenylene comprising bis terminal
3 alkoxy groups is to be incorporated into a monomer, R² is selected from
4 the group consisting of t-butyl groups, isopropyl groups, secondary butyl
5 groups, methyl groups, and phenyl groups; and,
6 when said bis 1,4 [4-alkoxybenzoyloxy]-R²-phenylene is to be incorporated
7 into a dimer, R² is selected from the group consisting of bulky organic
8 groups and groups having a bulk less than methyl groups.

1 153. The method of claim 1 wherein said first terminal functionality and
2 said second terminal functionality are independently selected from the group
3 consisting of polymerizable groups, hydroxyl groups, amino groups, sulfhydryl
4 groups, halogen atoms, H-(CH₂)_n-O- groups, Cl(CH₂)_n-O- groups, Br(CH₂)_n-O-
5 groups, I(CH₂)_n-O-, wherein n is from about 2 to about 12 and CH₂ independently can
6 be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon
7 atoms separate said oxygen or said ester group.

1 154. The method of claim 3 wherein said first terminal functionality and
2 said second terminal functionality are independently selected from the group
3 consisting of polymerizable groups, hydroxyl groups, amino groups, sulfhydryl
4 groups, halogen atoms, $\text{H}-(\text{CH}_2)_n\text{-O-}$ groups, $\text{Cl}(\text{CH}_2)_n\text{-O-}$ groups, $\text{Br}(\text{CH}_2)_n\text{-O-}$
5 groups, $\text{I}(\text{CH}_2)_n\text{-O-}$, wherein n is from about 2 to about 12 and CH_2 independently can
6 be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon
7 atoms separate said oxygen or said ester group.

1 155. The method of claim 27 wherein said first terminal functionality and
2 said second terminal functionality are independently selected from the group
3 consisting of polymerizable groups, hydroxyl groups, amino groups, sulfhydryl
4 groups, halogen atoms, $\text{H}-(\text{CH}_2)_n\text{-O-}$ groups,, $\text{Cl}(\text{CH}_2)_n\text{-O-}$ groups, $\text{Br}(\text{CH}_2)_n\text{-O-}$
5 groups, $\text{I}(\text{CH}_2)_n\text{-O-}$, wherein n is from about 2 to about 12 and CH_2 independently can
6 be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon
7 atoms separate said oxygen or said ester group.

1 156. The method of claim 28 wherein said first terminal functionality and
2 said second terminal functionality are independently selected from the group
3 consisting of polymerizable groups, hydroxyl groups, amino groups, sulfhydryl
4 groups, halogen atoms, $\text{H}-(\text{CH}_2)_n\text{-O-}$ groups, $\text{Cl}(\text{CH}_2)_n\text{-O-}$ groups, $\text{Br}(\text{CH}_2)_n\text{-O-}$
5 groups, $\text{I}(\text{CH}_2)_n\text{-O-}$, wherein n is from about 2 to about 12 and CH_2 independently can
6 be substituted by oxygen, sulfur, or an ester group; provided that at least 2 carbon
7 atoms separate said oxygen or said ester group.