

POLYCARBONATE AND POLYESTER COMPOSITIONS

This invention relates to polycarbonates, polyesters, and polyestercarbonates prepared from at least one aromatic diol, wherein a portion or all of the aromatic diol used in their preparation is a stilbene diol.

Certain polymers derived from stilbene diols are known and are described, for example, in Cebe et al., Polym. Preprints, Vol. 33, p. 331 (1992), Bluhm et al., Mol. Cryst. Liq. Cryst., Vol. 239, p. 123 (1994), and Cheng et al., Macromolecules, Vol. 27, p. 5440 (1994), which describe the preparation of mixed aromatic-aliphatic polycarbonates based on stilbene diols and C₄₋₁₂ alpha,omega-alkanediols. Percec et al., J. Polym. Sci. Polym. Lett., Vol. 22, p. 637 (1984) and J. Polym. Sci. Part A: Polym. Chem., Vol. 25, p. 405 (1987) report the synthesis of mixed aromatic-aliphatic polyethers via the reaction of 4,4'-dihydroxy-alpha-methylstilbene with C₁₋₁₁ alpha,omega-dibromoalkanes. Blumstein et al., Mol. Cryst. Liq. Cryst., Vol. 49, p. 255 (1979) and Polym. Journal, Vol. 17, p. 277 (1985) describe mixed aromatic-aliphatic polyesters from stilbene diols and alpha,omega-alkanedicarboxylic acids. Roviello and Sirigu, Makromol. Chem., Vol. 180, p. 2543 (1979), Makromol. Chem., Vol. 183, p. 409 (1982) and Makromol. Chem., Vol. 183, p. 895 (1982) report the preparation of mixed aromatic-aliphatic thermotropic liquid crystalline polyesters from 4,4'-dihydroxy-alpha-methylstilbene and C₈₋₁₄ alpha,omega-alkanedicarboxylic acids. Sato, J., Polym. Sci.: Part A: Polym. Chem., Vol. 26, p. 2613 (1988) reports the synthesis of mixed aromatic-aliphatic polyesters using 4,4'-dihydroxy-alpha,alpha'-diethylstilbene and adipoyl chloride, sebacoyl chloride, and mixtures of adipoyl and sebacoyl chlorides. However, the physical properties and melt characteristics of such polymers may be less than desirable for certain applications.

In one aspect, this invention is a polycarbonate, polyester, or polyestercarbonate composition prepared from a reaction mixture comprising at least one diol and at least one carbonate precursor or ester precursor, wherein

- (a) at least 95 mole percent of the carbonate precursor or ester precursor present in the reaction mixture is selected from
- (i) dialkyl carbonates, diarylcarbonates, carbonyl halides, or bis(trialkyl) carbonates;
 - (ii) aromatic dicarboxylic acids, hydroxybenzoic acids, hydroxynaphthoic acids, hydroxybiphenyl acids, hydroxycinnamic acids, or the halides or metal salts of such acids; or
 - (iii) oligomers and polymers of (i) or (ii) containing carbonate or ester groups, which are prepared by contacting an excess over stoichiometry of at least one compound selected from (i) or (ii) with at least one monol or diol under reaction conditions sufficient to form the corresponding oligomer or polymer; or

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(b) at least 95 mole percent of the diol present in the reaction mixture consists of one or more aromatic diols, at least 10 mole percent of which consists of one or more stilbene diols.

Applicants have discovered that the composition of the invention has an advantageous thermal resistance, melting temperature, tensile and flexural properties, and/or resistance to thermal embrittlement. Moreover, those polymers of the invention which are thermotropic liquid crystalline also have an advantageous temperature range for liquid crystallinity, melt processibility, coefficient of thermal expansion, ignition resistance, solvent resistance, and/or barrier properties. These and other advantages of the invention will be apparent from the description which follows.

The polymeric composition of the invention may be prepared by any method suitable for the preparation of polycarbonate, polyester, or polyester carbonate polymers, so long as at least 95 mole percent of the diol present in the polymerization reaction mixture consists of one or more aromatic diols, and at least 10 mole percent of the aromatic diols consists of one or more stilbene diols. Such methods include interfacial, solution, and melt polymerization processes. Further, the polymeric composition of the invention may be prepared as a homopolymer, or as a random or block copolymer of the various monomers described below. The term "reaction mixture" as used herein refers to the mixture of monomers which are polymerized to form the composition of the invention, utilizing any of the polymerization methods described in any of the references cited herein.

The composition of the invention preferably comprises repeating units of the formulas:



and optionally



wherein R independently in each occurrence is the divalent nucleus of an aromatic diol, X is selected from: $-C(O)-$, $-C(O)-R^1-C(O)-$, or a mixture thereof, R^1 independently in each occurrence is the divalent nucleus of a difunctional aromatic carboxylic acid, and R^2 is the divalent nucleus of an aromatic hydroxy carboxylic acid. As indicated by the above formulas, other monomers such as hydroxy carboxylic acids may also be present in the polymerization reaction mixture, in addition to the diols and carbonate precursors. The term "divalent nucleus" as used herein refers to the compound described, minus its pendant hydroxyl and/or carboxyl groups.

When the polymeric composition of the invention is a polycarbonate, it may be prepared by the reaction of an aromatic diol or mixtures of aromatic diols with a carbonate precursor. The term "carbonate precursor" as used herein refers to carbonyl halides, diaryl carbonates, dialkyl carbonates, bis(trihaloalkyl)-carbonates such as triphosgene, bis(haloformates), and other compounds which will react with hydroxyl groups to form carbonate linkages $(-O-C(O)-O-)$. Examples of suitable carbonyl halides include carbonyl

bromide, carbonyl chloride ("phosgene") and mixtures thereof. Suitable haloformates include the bischloroformates of dihydric phenols such as bisphenol A. Preferably, the carbonate precursor is phosgene or diphenyl carbonate, and is most preferably diphenyl carbonate. Examples of suitable methods for preparing polycarbonates are set forth in "Polycarbonates,"
5 Encyclopedia of Polymer Science and Engineering (2nd Edition), Vol. 11, pp. 648-718 (1988); U.S. Patent Nos. 5,142,018; 5,034,496; 4,831,105; 4,543,313; 3,248,414; 3,153,008; 3,215,668; 3,187,065; 3,028,365; 2,999,846; 2,999,835; 2,970,137; 2,964,974; and 1,991,273.

When the polymeric composition of the invention is a polyester, it may be prepared by the reaction of an aromatic diol or a reactive derivative thereof (such as the
10 corresponding diacetate), with an ester precursor. The term "ester precursor" as used herein refers to C_{8-40} dicarboxylic acids or reactive derivatives thereof (such as esters thereof or the corresponding acid halides), which will react with hydroxyl groups to form ester linkages ($-O-C(O)-R^1-C(O)-O-$, wherein R^1 is the divalent nucleus of the ester precursor). Preferably, the ester precursor is an aromatic dicarboxylic acid.

15 A portion of the ester component in these polymeric compositions may optionally be derived from hydroxycarboxylic acids or reactive derivatives thereof, either by reaction with the other monomers or self-condensation, to provide repeat units of Formula (II): $-[R^2-C(O)-O]-$, wherein R^2 is the divalent nucleus of a hydroxycarboxylic acid. Examples of suitable methods for preparing polyesters are set forth in "Polyesters," Encyclopedia of
20 Polymer Science and Engineering (2nd Edition), Vol. 12, pp. 1-75 (1988); "Liquid Crystalline Polymers," Encyclopedia of Polymer Science and Engineering (2nd Edition), Vol. 9, pp. 1-61 (1988); "Polyesters, Mainchain Aromatic," Encyclopedia of Polymer Science and Engineering (2nd Edition), Vol. 1, pp. 262-279; U.S. Patent Nos. 5,268,443; 5,237,038; 5,233,013; 5,221,730; 5,175,237; 5,175,326; 5,110,896; 5,071,942; 5,037,938; 4,987,208; 4,946,926; 4,945,150; and
25 4,985,532.

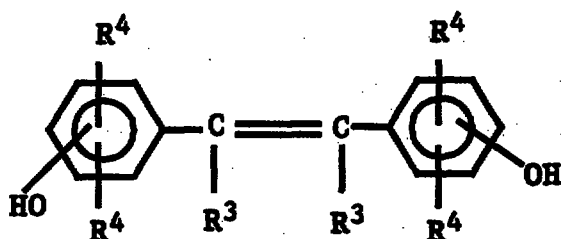
Similarly, when the polymeric composition of the invention is a polyestercarbonate, it may be prepared by the reaction of an aromatic diol with a combination of a carbonate precursor and an ester precursor as described above. Suitable methods for the preparation of polyestercarbonates are described in U.S. Patent Nos 5,045,610; 4,398,018;
30 4,388,455; 4,374,973; 4,371,660; 4,369,303; 4,360,656; 4,355,150; 4,330,662; 4,287,787; 4,260,731; 4,255,556; 4,252,939; 4,238,597; 4,238,596; 4,194,038; 4,156,069; 4,107,143; 4,105,633; and 3,169,121; and articles by Kolesnikov et al. published in Vysokomol Soedin as B9, p. 49 (1967); A9, p. 1012 (1967); A9, p. 1520 (1967); and A10, p. 145 (1968).

In the preparation of the composition of the invention, at least 95 mole percent
35 of the carbonate precursor or ester precursor present in the reaction mixture is
(i) dialkyl carbonates, diarylcarbonates, carbonyl halides, or bis(trihaloalkyl) carbonates;

(ii) aromatic dicarboxylic acids, hydroxybenzoic acids, hydroxynaphthoic acids, hydroxybiphenyl acids, hydroxycinnamic acids, and the halides or metal salts of such acids; or

(iii) oligomers and polymers of (i) or (ii) containing carbonate or ester groups, which are prepared by contacting an excess over stoichiometry of at least one compound selected from (i) or (ii) with at least one monol or diol under reaction conditions sufficient to form the corresponding oligomer or polymer. The term "oligomer" as used herein includes monoesters, diesters, monocarbonates, and dicarbonates of the monol or diol.

Suitable stilbene diols for use in the preparation of the polymeric composition of the invention include those of the formula:



wherein R^3 independently in each occurrence is selected from hydrogen, C_{1-8} alkyl, chlorine, bromine, or cyano, but is preferably hydrogen or C_{1-8} alkyl; R^4 independently in each occurrence is selected from hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, cyano, nitro, carboxamide, carboximide, or $R^5-C(O)-$, wherein R^5 is C_{1-8} alkyl or aryloxy, but is preferably hydrogen or C_{1-8} alkyl. Preferably, the phenolic groups are in a "trans" configuration the double bond. Preferably, the stilbene diol is 4,4'-dihydroxystilbene; 4,4'-dihydroxy- α -methylstilbene; 4,4'-dihydroxy- α,α' -dimethylstilbene; or 4,4'-dihydroxy- α,α' -diethylstilbene.

The stilbene diols described above may be prepared by any suitable method. For example, the diol is prepared from a phenol and a carbonyl-containing precursor, using any of the procedures described by S. M. Zaher et al., Part 3, *J. Chem. Soc.*, pp. 3360-3362 (1954); V. Percec et al., *Mol. Cryst. Liq. Cryst.*, Vol. 205, pp. 47-66 (1991); Singh et al., *J. Chem. Soc.*, p. 3360 (1954), or Hefner et al., U.S. Patent No. 5,414,150. If desired, color bodies, or color forming bodies, may be removed from the stilbene diols by contacting them with an aqueous solution of one or more compounds selected from alkali metal carbonates, alkali earth metal carbonates, alkali metal bicarbonates (such as sodium bicarbonate), or alkaline earth metal carbonates. The stilbene diol(s) used to prepare the composition of the invention preferably have a 4,4'-isomeric purity of at least 95 mole percent, more preferably at least 98 mole percent and most preferably at least 99 mole percent.

In addition to the stilbene diol, one or more additional aromatic diols may also be used to prepare the composition of the invention. Suitable aromatic diols include any aromatic diol which will react with a carbonate precursor or ester precursor. Preferred diols include 2,2-bis(4-hydroxyphenyl)propane ("bisphenol A"); 9,9-bis(4-hydroxyphenyl)fluorene; hydroquinone; resorcinol; 4,4'-dihydroxybiphenyl; 4,4'-thiodiphenol; 4,4'-oxydiphenol; 4,4'-sulfonyldiphenol; 4,4'-dihydroxybenzophenone; 4,4''-dihydroxyterphenyl; 1,4-dihydroxynaphthalene; 1,5-dihydroxynaphthalene; 2,6-dihydroxynaphthalene; bis(4-hydroxyphenyl)methane ("bisphenol F"); and inertly substituted derivatives thereof, as well as mixtures thereof. Preferably, the diol is 2,2-bis(4-hydroxyphenyl)propane ("bisphenol A").

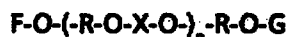
In the preparation of the composition of the invention, at least 95 mole percent of the diols present in the reaction mixture consist of one or more aromatic diols. Preferably, at least 98 mole percent, and more preferably 100 mole percent of such diols are aromatic diols. Further, at least 10 mole percent of the aromatic diol present in the reaction mixture consists of one or more stilbene diols. Preferably, at least 25 mole percent, and more preferably at least 50 mole percent of such aromatic diols are stilbene diols.

Examples of aromatic dicarboxylic acids which may be used to prepare polyester or polyester carbonate compositions of the invention include terephthalic acid; isophthalic acid; 2,6-naphthalenedicarboxylic acid; 1,4-naphthalenedicarboxylic acid; 1,5-naphthalene-dicarboxylic acid; 4,4'-biphenyldicarboxylic acid; 3,4'-biphenyldicarboxylic acid; 4,4'-terphenyldicarboxylic acid; 4,4'-stilbenedicarboxylic acid; 4,4'-dicarboxy-alpha-methylstilbene; inertly substituted derivatives thereof, as well as mixtures thereof.

Examples of hydroxycarboxylic acids that may be used to prepare the polyester and polyester carbonate polymeric compositions of the present invention include 4-hydroxybenzoic acid; 3-hydroxybenzoic acid; 6-hydroxy-2-naphthoic acid; 7-hydroxy-2-naphthoic acid; 5-hydroxy-1-naphthoic acid; 4-hydroxy-1-naphthoic acid; 4-hydroxy-4'-biphenylcarboxylic acid; 4-hydroxy-4'-carboxydiphenyl ether; 4-hydroxycinnamic acid; inertly substituted derivatives thereof, as well as mixtures thereof.

Processes for the preparation of polycarbonates, polyesters, and polyester carbonates typically employ a chain stopping agent during the polymerization step to control molecular weight. The amount of chain stopping agent has a direct effect on both the molecular weight and the viscosity of the polycarbonate, polyester, or polyester carbonate prepared. Chain stopping agents are monofunctional compounds which react with a carbonate or ester precursor site on the end of the polymer chain and stop the propagation of the polymer chain. Examples of suitable chain stopping agents include monofunctional aromatic alcohols, thiols, and amines, as well as mixtures thereof. Preferably, the chain stopping agent is a monofunctional aromatic alcohol, thiol, amine, aliphatic alcohol, aromatic carboxylic acid, aliphatic carboxylic acid, or a mixture thereof.

The compositions of the present invention are preferably of the following formula:



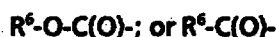
and optionally contain repeat units of Formula (II): $(\text{-R}^2\text{-C(O)-O-})_n$; and/or end groups of the

5 formulas:



wherein R, X, R¹ and R² have the descriptions hereinbefore provided; n is a whole number from 5 to 300; and F and G are, independently, either hydrogen or other terminating groups common to polycarbonates, polyesters carbonates, or polyesters. Preferably, F and G are

10 represented by the formulas:



wherein R⁶ is hydrogen, halogen, or the nucleus of an alkyl, aryl, or alkyl-substituted aryl alcohol or carboxylic acid.

The polymers of the present invention preferably have a weight average
15 molecular weight (Mw, determined by size exclusion chromatography using a bisphenol A polycarbonate calibration curve) of at least 10,000, more preferably at least 20,000. Preferred polymers according to the present invention have inherent viscosities, measured in methylene chloride (for an amorphous polymer) at 0.5 grams per deciliter (g/dL) and 25°C, or in pentafluorophenol (for a crystalline or liquid crystalline polymer) at 0.1 g/dL and 45°C, of at
20 least 0.2 dL/g and more preferably at least 0.35 dL/g.

Liquid crystalline polymeric compositions may be identified using one or more standard techniques, such as heating the composition on a differential scanning calorimeter and characterizing it in the melt state by optical microscopy under cross-polarized light. Thermotropic liquid crystalline polymers will exhibit optical anisotropy upon melting. Other
25 techniques which may be used to characterize the polymer as liquid crystalline include scanning electron microscopy, X-ray diffraction, visible light scattering techniques, electron beam diffraction, infrared spectroscopy, and nuclear magnetic resonance. If the composition is liquid crystalline, it preferably has nematic ordering in the liquid crystalline melt state.

As mentioned above, the compositions of the invention advantageously have a
30 relatively high thermal resistance, melting temperature, tensile and flexural properties, and/or resistance to thermal embrittlement. Moreover, those polymers of the invention which are thermotropic liquid crystalline also advantageously possess a broad temperature range for liquid crystallinity, good melt processibility, a low coefficient of thermal expansion, a high ignition resistance, high solvent resistance, and/or good barrier properties. The thermal
35 resistance of the composition may be characterized by its Vicat softening temperature and the temperature at which it may be distorted under load, as illustrated in Example 2. The tensile and flexural properties of the composition may be characterized and measured in accordance with ASTM D-638, as illustrated in the examples. The composition's resistance to thermal

embrittlement refers to its tendency to become brittle at elevated temperature, and may be characterized by measurement of its post yield stress drop, as illustrated in Example 7.

The composition of the invention, when thermotropic liquid crystalline, also preferably has thermal characteristics which permit it to be readily processed in the liquid crystal state when heated above its melt temperature. The temperature range over which such polymers may be processed above their melt temperature in the liquid crystal state is preferably as broad as possible, but is preferably at least 25°C, more preferably at least 50°C, and is most preferably at least 100°C. In most instances, the composition will become isotropic above this range, in which case the range may be expressed as the difference between the clearing temperature (T_{cl}) and the melt temperature (T_m) of the composition. The clearing temperature is the temperature at which the composition undergoes a transition from the anisotropic liquid crystalline state to an isotropic state (see, for example, The Encyclopedia of Polymer Science and Engineering, Vol. 9, p. 55 (1988)).

The melt processibility of the polymeric composition may be characterized by its melt temperature and its melt viscosity, as illustrated in the examples. The melt temperature of the composition (T_m , as determined by Differential Scanning Calorimetry) when thermotropic liquid crystalline, is preferably at least 200°C, more preferably at least 250°C, but is preferably no greater than 350°C.

The coefficient of thermal expansion of the composition of the invention may be measured in accordance with ASTM D-2236, as illustrated in the Examples below. The ignition resistance of the polymers may be measured by determining the Limiting Oxygen Index of the composition, by testing the composition in accordance with Underwriters Laboratories' test number UL-94, or by measuring the char yield of the composition by thermal gravimetric analysis. The solvent resistance of the composition of the invention may be characterized as shown in the examples.

The barrier properties of the composition of the invention may be measured in accordance with ASTM D-3985 (oxygen transmission rate) and ASTM F-372 (carbon dioxide and water vapor transmission rate).

The composition of the invention may be subjected to post-condensation in the solid phase (also known as solid-state advancement), preferably under reduced pressure, at a temperature in the range from 150°C to 350°C. After 1 to 24 hours, the molecular weight has increased and the resulting polymers exhibit further improved properties. The composition of the present invention may be fabricated using any of the known thermoplastic molding procedures, including compression molding, injection molding, and extrusion to provide fabricated articles, including moldings, boards, sheets, tubes, fibers, and films. Procedures that may be employed to maximize the orientation of the liquid crystal moieties contained in fabricated articles from the polymers of the invention are summarized in U.S. Patent No. 5,300,594, as well as the references cited therein.

The composition of the present invention can also be employed with other thermoplastic polymers to prepare thermoplastic polymer blends. Suitable thermoplastics for this purpose include polycarbonates, polyesters, polyethers, polyetherketones, polysulfides, polysulfones, polyamides, polyurethanes, polyimides, polyalkylenes such as polyethylenes and polypropylenes, polystyrenes, copolymers thereof and mixtures thereof. The polymers of this invention may, in addition to being used for molding purposes, be employed as the base for preparing thermoplastic molding compositions by being compounded with antioxidants, antistatic agents, inert fillers and reinforcing agents such as glass fibers, carbon fibers, talc, mica, and clay, hydrolytic stabilizers, colorants, thermal stabilizers, flame retardants, mold release agents, plasticizers, UV radiation absorbers, and nucleating agents as described in U.S. Patent Nos. 4,945,150 and 5,045,610 and the other references cited above.

The following examples are given to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are given by weight.

Example 1 - Preparation of Polycarbonate of 4,4'-Dihydroxy-alpha-methylstilbene (DHAMS)

The polymerization was run in a 1 L single-neck round-bottom flask fitted with a two-neck adapter upon which were mounted a glass paddle stirrer and a 13 centimeter (cm) Vigreux distillation column, distillation head with a thermometer, condenser and a receiver. DHAMS (1.79 mol, 403.6 g) and diphenylcarbonate (1.93 mol, 412.7 g) were added to the reaction flask. The apparatus was evacuated and refilled with nitrogen three times. The flask was immersed in a molten salt bath preheated to 220°C. When the solid reactants had melted to form a molten reaction mass, stirring was started and an aqueous solution of lithium hydroxide (0.82 mL, 0.06 M) was added as a catalyst. The reaction temperature was raised to 290°C over a period of 1 hour and the pressure was reduced from atmospheric pressure to 2×10^{-3} atmospheres. The latter pressure was maintained for one hour at 290°C. After an additional 5 minutes the reaction mass formed a ball on the stirrer shaft. The vacuum was then released under nitrogen and the reaction vessel was removed from the salt bath. The reaction apparatus was cooled and disassembled. The distillation receiver contained 337 g of phenol. The flask was broken away from the opaque chalk-white polycarbonate plug. The plug was sawed into chunks and then ground in a Wiley mill. The product was dried in a vacuum oven at 100°C for 2 hours to give 408 g of product (91 percent yield).

The polycarbonate had an inherent viscosity (IV) of 2.6 dL/g, measured at 45°C using a solution of 0.1 g of polycarbonate in 100 mL of pentafluorophenol. Differential scanning calorimetry (DSC), conducted at 20°C/minute using a Du Pont Instruments DSC 2910, showed a peak melting point of 273°C (first heating scan, run from 25°C to 320°C) and a crystallization temperature of 202°C (first cooling scan, run from 320°C to 50°C). A second heating scan showed a peak endotherm at 272°C, and a second cooling scan showed a crystallization temperature at 194°C. When the initial heating scan was run from 25°C to 400°C,

a second endotherm was observed at 375°C. Examination by hot stage cross-polarized microscopy (described hereinafter) indicated that the first endotherm was a solid crystalline to nematic liquid crystalline transition, and the second endotherm was a nematic liquid crystalline to isotropic liquid clearing transition.

- 5 The ^1H NMR and ^{13}C NMR spectra of the DHAMS polycarbonate are determined in pentafluorophenol at 45°C. The ^1H NMR (300 MHz) spectrum of the homopolycarbonate showed the presence of aliphatic, aromatic and vinylic hydrogen atoms. The infrared spectrum showed the presence of C=O, C=C, and C-O groups. Apparent molecular weights were determined by gel permeation chromatography (GPC) using refractive index detection.
- 10 Calibration was done using both BA (BA) polycarbonate and narrow molecular weight distribution polystyrene, with chloroform as the mobile phase. Sample preparation was done by dissolution of 40 mg sample in 1 mL pentafluorophenol at 45°C followed by addition of 10 mL chloroform. Using BA polycarbonate for calibration, the DHAMS polycarbonate sample had $M_w = 66,000$ and $M_n = 13,000$. Using polystyrene as the calibration, the DHAMS
- 15 polycarbonate had $M_w = 154,000$ and $M_n = 20,000$.

Characterization by Optical Microscopy Under Crosspolarized Light

- The apparatus used for determining optical anisotropy included a THM 600 hot stage (Linkham Scientific Instruments LTD, Surrey, England) and a Nikon Optiphot Microscope equipped with crossed-polarizers and a 35 mm camera (Nikon Instrument Group, Nikon, Inc.,
- 20 Garden City, N.Y). Observation of a bright field at temperatures above the melting point indicated that the DHAMS polycarbonate melt was optically anisotropic. The sample was placed on the programmable hot stage and a heating rate of 50°C/minute was used initially from 25°C to 180°C, then 10°C/minute was used from 180°C to 250°C and then 5°C/minute was used from 250°C to 300°C. Observation of the samples showed a nematic phase at room
- 25 temperature and a nematic phase upon melting. The polymer formed a turbid melt that showed strong shear opalescence. The following observations were made for this DHAMS polycarbonate sample, using the polarizing microscope.

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	<u>Temperature (°C)</u>	<u>Observations</u>
	25	white opaque solid
	150	white opaque solid
	180	compressed between coverslip and slide
5	260	highly birefringent, nematic texture, viscous fluid
	290	highly birefringent, nematic texture, flow directed domains
	300	anisotropic melt, still passes crosspolarized light

The sample remains anisotropic above 300°C, indicating that DHAMS

- 10 polycarbonate was liquid crystalline. Clearing (transition from liquid crystalline to isotropic phase) was not observed until 370°C.

Solubility Characterization

- 15 The thermotropic liquid crystalline DHAMS polycarbonate prepared in this example was insoluble in conventional organic solvents both at room temperature and elevated temperatures. Solvents that do not dissolve this polycarbonate include methylene chloride, chloroform, carbon tetrachloride, tetrahydrofuran, acetone, N,N-dimethylacetamide, dimethylsulfoxide, pyridine, and trifluoroacetic acid/methylene chloride (4/1 volume ratio). The polycarbonate was soluble in pentafluorophenol at high dilutions (0.1g/dL).

Melt Viscosity Determination

- 20 The melt viscosity of the DHAMS polycarbonate sample was determined using an Instron 3211 capillary rheometer with capillary length of 1.0087 inch, capillary diameter of 0.05005 inch, a shear rate range of 3.5 to 350 sec⁻¹, and a temperature of 290°C. The samples for the rheometer were prepared by placing a pre-dried, (100°C vacuum oven dried) polymer sample (1 g) in a stainless steel die, pressing in a hydraulic press at a platen pressure of 3,000
25 pounds for a few minutes and obtaining cylindrical pellets. The melt viscosity of DHAMS polycarbonate was determined to be 810 poise at 100 sec⁻¹ and 250 poise at 400 sec⁻¹.

Thermogravimetric Analysis (TGA)

- 30 TGA is run using a Du Pont 2100 thermal analyzer, a temperature scan range from 25°C to 1000°C, a heating rate of 10°C/minute, and a nitrogen purge. The residue remaining at 1000°C, also known as the char yield, is 38 percent for DHAMS polycarbonate. The significance of char yield and its relation to ignition resistance were discussed by Van Krevelen, Properties of Polymers, p. 731 (Third Edition, 1990).

Example 2 - Injection Molding and Properties of DHAMS Polycarbonate

- 35 DHAMS polycarbonate, prepared according to the procedure of Example 1, was ground in a Thomas-Wiley model 4 laboratory mill, dried at 100°C in a vacuum oven for 2 hours, and then injection molded using an Arburg injection molding machine. Standard 0.125 inch thick test specimens were injection molded at a barrel temperature of 300°C, a mold temperature of 125°C, and using 275 bars of injection pressure. Tensile strength at break (Tb),

tensile modulus (TM), elongation at break (Eb), flexural strength (FS), and flexural modulus (FM) were determined according to American Society for Testing and Materials (ASTM) test method D-638. The notched Izod impact strength was determined according to ASTM D-256 wherein a 0.01 inch notch radius was employed. Vicat softening temperature for the polymer was determined according to ASTM D-1525 using a 1 kg load. The coefficient of linear thermal expansion (CLTE) in the flow direction was measured according to ASTM D-2236. Limiting oxygen index (LOI) was determined according to ASTM D-2863-87. UL-94 determinations of flammability resistance was conducted as specified by Underwriters Laboratories. Water absorption was measured at 25°C after 24 hours immersion time. Specific gravity was measured according to ASTM D-570. These results were as follows: Specific Gravity - 1.27; H₂O Absorption (percent) - 0.002; LOI (percent oxygen) - 37; UL-94 Rating V-0; CLTE (ppm/°C) - 25 to 35; Vicat (°C) - 188; Tb (psi) - 15,970; TM (psi) 575,800; Eb (percent) - 5; FS (psi) - 18,970; FM (psi) - 656,600; N. Izod (ft-lb/in) - 8.8. The thermal resistance of DHAMS polycarbonate was also evaluated using a 0.025 inch diameter probe carrying a load of 10 g. Penetration of the sample was not observed until a temperature of 270°C was reached.

Example 3 - Solid State Advancement of DHAMS Polycarbonate

A sample of DHAMS polycarbonate having an IV of 0.42 dL/g (measured in pentafluorophenol at 0.1g/dL and 45°C) was synthesized by the general procedure of Example 1. DSC analysis showed a melting temperature of 231°C and a crystallization temperature of 157°C, determined during the first heating and cooling cycles according to the procedure described above. The DHAMS polycarbonate was then solid state advanced with stirring at 220°C under a reduced pressure of 2×10^{-4} atmospheres for 48 hours, resulting in an increase in IV to 2.2 dL/g, a melting point at 271°C, and a crystallization temperature of 192°C.

Example 4 - Preparation of Mixture of DHAMS Polycarbonate and Glass Fibers

DHAMS polycarbonate (prepared as in Example 1) (417 g) was dry mixed with Owens-Corning glass fibers (125 g, 0.125 inch nominal length, #492). The mixture was then compounded using a Brabender conical twin screw extruder (counter-rotating) at 40 rpm screw speed, with the feed zone at 255°C and all other zones at 300°C. The mixture was starve-fed to the extruder using a K-Tron volumetric screw, having a feeder setting at 10.0, venting under vacuum of any volatiles from the polymer melt, and a die was maintained. The measured torque was approximately 2,500 meter-gram and the head-pressure was less than 2,000 psi. As the mixture exited the die it was quenched with a water spray and cut into pellets with a conventional strand cutter. The resulting pellets were dried for approximately 16 hours in a vacuum oven set at 100°C and then were injection molded into standard test specimens (as specified by ASTM D-638 for determining tensile properties) on an Arburg molding machine using a barrel temperature of 300°C, a mold temperature of 125°C, and 275 bars of injection pressure.

Example 5 - Preparation of a Mixture of DHAMS Polycarbonate and BA Polycarbonate

DHAMS polycarbonate with an IV of 1.5 dL/g (measured in pentafluorophenol at 0.1 g/dL and 45°C) and BA polycarbonate with a Condition O melt flow rate of 10 g/10 minutes were each separately cryogenically ground to a fine powder. A portion (0.5011 g) of the DHAMS polycarbonate and a portion (4.50 g) of the BA polycarbonate were combined and mixed. The resulting mixture (4.76 g) was added over an 8 minute period to the stirred reservoir of an injection molder which was preheated to 260°C. After addition of the mixture was completed, the stirred mixture was maintained for an additional 12 minutes at the 260°C temperature prior to shutting off the stirring. The mixture was then injected into a 3 inch by 0.5 inch by 0.125 inch stainless steel mold which was preheated to 260°C.

The resulting molding was allowed to slowly cool to 23°C before removing it from the molding machine. The molded specimen was opaque when it was removed. The flashing recovered from the edges of the injection molded mixture was examined by optical microscopy under cross-polarized light at both 75X and 300X magnifications. For the flashing, birefringent fibers were observed at both magnifications and were oriented in the flow direction in an isotropic matrix. A sample of the residual mixture remaining in the reservoir of the injection molder was removed and heated to 260°C using a hot stage and then examined by optical microscopy under cross-polarized light. Birefringent fibers were observed at both magnifications and these fibers were randomly oriented in an isotropic matrix.

Example 6 - Preparation of DHAMS/BA Copolycarbonates Using Melt Transesterification

The copolymerization was run in a 250 mL, single-neck, round-bottom flask, fitted with a two-neck adapter upon which were mounted a glass paddle stirrer and a 13 centimeter (cm) Vigreux distillation column, distillation head with a thermometer, condenser and a receiver. DHAMS (0.11 moles, 24.19 grams), BA (0.012 moles, 2.71 grams) and diphenylcarbonate (0.12 moles, 25.46 grams) were added to the reaction flask. The apparatus was evacuated and refilled with nitrogen three times. The flask was immersed in a molten salt bath preheated to 220°C. When the solid reactants were melted to form a molten reaction mass, stirring was started and an aqueous solution of lithium hydroxide was added as a catalyst (0.36 mL, 0.06 M).

The reaction temperature was raised to 265°C over a period of one hour from atmospheric pressure to 2×10^{-3} atmospheres. The latter pressure was maintained for 1 hour at 265°C. After an additional 5 minutes the reaction mass formed a ball on the stirrer shaft. The vacuum was then released under nitrogen and the reaction vessel was removed from the salt bath. The reaction apparatus was cooled and disassembled. The flask was broken away from an opaque chalk-white copolycarbonate plug. The plug was sawed into chunks and then ground in a Wiley mill. The copolycarbonate had an inherent viscosity of 0.91 dL/g which was measured at 45°C using a solution of 0.1 g of polycarbonate in 100 mL of pentafluorophenol. The peak melting point was 250°C on the first heating scan as measured by differential



scanning calorimetry (DSC) on a sample run at 10°C/minute. A second heating scan showed only a T_g at 84°C and no melting point transition is observed.

The copolycarbonate was characterized by optical microscopy under cross-polarized light. Observation of a bright field at temperatures above the melting point indicated that the copolycarbonate melt was optically anisotropic.

Additional copolycarbonates of DHAMS and BA were prepared according to the general procedure described above. These copolycarbonates were based on DHAMS/BA molar ratios of 90/10 to 50/50. The copolycarbonates were characterized by DSC for the determination of glass transition temperature (T_g) and melting temperature (T_m), IV, TGA (percent char), and optical microscopy under cross-polarized light as described above. These results are shown in Table I.

Table I

	<u>DHAMS/BA Molar Ratio</u>	<u>IV (dL/g)</u>	<u>T_g (°C)</u>	<u>T_m (°C)</u>	<u>TGA % Char</u>	<u>Nematic Melt</u>
15	90/10	0.91 ^a	84	250	35	Yes
	75/25	0.36	105	216 ^b	31	Yes
	70/30	0.59	124	213 ^b	31	No
	65/35	0.38	130	210 ^b	30	No
20	60/40	0.59	134	218 ^b	30	No
	50/50	0.31	137	— ^c	29	No

^a Run in pentafluorophenol at 45°C.

^b After annealing 2 to 12 hours at 175°C under nitrogen.

^c No melting transition observed.

Example 7 - Preparation of DHAMS/BA (50/50 and 25/75 Molar Ratio) Copolycarbonates Using Solution Process

The following procedure was used to prepare a DHAMS/BA (50/50 molar ratio) copolycarbonate. A 2 L four-neck, round-bottom flask, equipped with a thermometer, condenser, phosgene/nitrogen inlet, and a paddle stirrer connected to a Cole Parmer servodyne was charged with DHAMS (26.80 g, 0.118 mol), BA (27.04 g, 0.118 mol), 4-tertbutylphenol (0.71 g, 4.7 mmol, a chain terminator), pyridine (48.5 g, 0.614 mol), and methylene chloride (0.5 L). The mixture was stirred at 250 rpm and slowly purged with nitrogen as phosgene (24.8 g, 0.251 mol) was bubbled in over 28 minutes while maintaining the reactor temperature at 17°C to 26°C. The reaction mixture was worked up by adding methanol (5 mL) and then a solution of 20 mL conc. HCl in 60 mL water.

After stirring for 15 minutes at 200 rpm, the mixture was poured into a 2 L separatory funnel. The methylene chloride layer was separated and washed further with a solution of 5 mL conc. HCl in 100 mL water, followed by 100 mL water, and then passed through a column (0.2 L bed volume) of macroporous cation-exchange resin. The product was isolated

- by adding the clear methylene chloride solution to a mixture of hexane (2 L) and acetone (0.2L) in an explosion resistant blender. The product was filtered, dried in a hood overnight, and then dried for 48 hours in a vacuum oven at 110°C. The dried product weighed 55.6 g and had an IV of 0.846 dL/g (determined in methylene chloride at 0.5 g/dL and 25°C). DSC analysis (first scan, 20°C/minute heating rate, scan from 50°C to 250°C) showed an extrapolated onset glass transition temperature (T_g) of 144°C. The second scan showed a T_g at 141°C. The ^1H NMR spectrum of the product was in agreement with the target copolycarbonate composition. Size exclusion chromatography using narrow fraction polystyrene standards gave the following molecular weight analysis: $M_w = 98,446$ and $M_w/M_n = 2.361$.

The general procedure of this example was used to prepare additional DHAMS/BA copolycarbonates having DHAMS/BA molar ratios of 50/50 and 25/75.

Compression Molding and Properties of DHAMS/BA Copolycarbonates

- Compression molded plaques of approximately 6 inch x 6 inch x 0.125 inch were prepared at molding temperatures 100°C above T_g using a Tetrahedron MTP-14 press. These transparent plaques were machined into test specimens. Tensile strength at yield (T_y), elongation at yield (E_y), and post-yield stress drop (PYSD) are determined according to ASTM D-638. A reduction in PYSD had been correlated with enhanced resistance to physical aging and fatigue, resulting in improved long-term property maintenance: see R. Bubeck et al., Polym. Eng. Sci., Vol. 24, p. 1142 (1984). IV, T_g , and notched Izod were determined as described above. These results are shown in Table II.

Table II

	DHAMS/BA Molar Ratio	IV (dL/g)	T_g (°C)	N.Izod (ft-lb/in)	T_y (psi)	E_y (%)	PYSD (%)
25	25/75	0.71	150	13.3	7,802	7.8	14.6
	50/50	0.64	135	11.2	7,459	7.6	8.1
	50/50	0.76	138	12.7	7,354	8.9	6.2

- Example 8 - Preparation of DHAMS/BA (75/25 Molar Ratio) Copolycarbonate Using Solution Process

- The same equipment as described in Example 7 was charged with DHAMS (40.30 g, 0.178 mol), BA (13.55 g, 0.059 mol), 4-tertbutylphenol (0.71 g, 4.7 mmol), pyridine (48.7 g, 0.616 mol), and methylene chloride (0.5 L). The mixture was stirred at 250 rpm and slowly purged with nitrogen as phosgene (24.4 g, 0.247 mol) was bubbled in over 21 minutes while maintaining the reactor temperature at 18°C to 26°C. The product began to precipitate from the reaction solution when 13 g of phosgene was added. The same workup procedure as



shown in Example 7 was followed, except that the product was not passed through a column of ion exchange resin. For this composition the product was a slurry in methylene chloride rather than a solution.

The product was isolated by adding the slurry to 3 L of methanol in an explosion resistant blender. The product was filtered, dried in a hood overnight, and then dried for 48 hours in a vacuum oven at 110°C. The product weighed 59.6 g and was insoluble in the following solvents that dissolve BA polycarbonate: methylene chloride, chloroform, tetrahydrofuran, dimethylformamide, and sym-tetrachloroethane. A compression molded plaque (approximately 0.02 inch thickness) prepared at 250°C (3 minutes molding time, 10,000 pounds platen pressure) was well-fused, opaque, creasable, insoluble in the solvents listed above, and does not stress crack when flexed and exposed to acetone. DSC analysis of the product showed a first scan T_g of 135°C and a melting endotherm from 175°C to 220°C with a transition peak at 194°C. A sample of this copolycarbonate was characterized by optical microscopy under crosspolarized light as described above. The sample was applied between a glass slide and a glass coverslip and then placed on the programmable hot stage of the microscope. A heating rate of 10°C/minute was employed and the following results were obtained:

<u>Temperature (°C)</u>	<u>Observations</u>
30	birefringent crystalline solid
145	slight softening observed when compressed between coverslip and slide
168	fuses to highly birefringent, opaque, viscous fluid as compressed
184	highly birefringent, viscous fluid
200	highly birefringent, viscous fluid, stir opalescent, nematic texture, orients with shear to give flow directed domains
245	some isotropic fluid observed
285	isotropic fluid containing scattered birefringent regions
291	isotropization complete

Example 9 - Preparation of DHAMS/9,9-Bis(4-hydroxy-phenyl)fluorene (BHPF) Copolycarbonate

The general procedure of Example 7 was used to prepare DHAMS/BHPF (75/25 molar ratio) copolycarbonate. The resulting copolycarbonate was insoluble in methylene chloride. DSC analysis showed a T_g at 173°C (first scan, 20°C/minute heating rate).

Example 10 - Preparation of Polyestercarbonate from DHAMS, Diphenyl Terephthalate, and Diphenyl Carbonate

The polymerization was run in a 250 mL single-neck, round-bottom flask, fitted with a two-neck adapter upon which are mounted a glass paddle stirrer and a 13 cm Vigreux distillation column, distillation head with a thermometer, condenser and a receiver. Diphenyl terephthalate (0.0143 mol, 3.64 g, an ester derivative of terephthalic acid), DHAMS (0.11 mol, 25.84 g), and diphenyl carbonate (0.10 mol, 22.02 g) was added to the reaction flask. The apparatus was evacuated and refilled with nitrogen three times. The flask was immersed in a molten salt bath preheated to 220°C. When the solid reactants had melted to form a molten reaction mass, stirring was started and lithium hydroxide (0.36 mL of 0.06 M aqueous solution) was added.

The reaction temperature was raised to 265°C over a period of one hour and the pressure was reduced from atmospheric pressure to 2×10^{-3} atmospheres. The latter pressure was maintained for 1 hour at 265°C. After an additional 5 minutes the reaction mass formed a ball on the stirrer shaft. The vacuum was then released under nitrogen and the reaction vessel was removed from the salt bath. The reaction apparatus was cooled and disassembled. The volume of phenol recovered was 20.1 mL. The flask was broken away from an opaque chalk-white product. The plug was sawed into chunks and then ground in a Wiley mill. The polyestercarbonate had an inherent viscosity of 1.05 dL/g (pentafluorophenol, 45°C, 0.1 g/dL). DSC analysis, conducted at a scan rate of 10°C/minute, showed a melting transition at 213°C.

Example 11 - Preparation of Polyester from 4,4'-Diacetoxy- α -methylstilbene (DAAMS) and Terephthalic Acid

The following procedure was used to convert DHAMS to DAAMS. To a single-neck, 500 mL, round-bottom flask, equipped with a condenser and nitrogen inlet, were added DHAMS (0.133 mol, 30 g) and acetyl chloride (0.665 mol, 48 mL) in methylene chloride (200 mL). The reaction mixture was refluxed for 3 hours and a clear solution was obtained, at which point by High Pressure Liquid Chromatography (HPLC) analysis the reaction had reached completion. The reaction mixture was cooled, and then concentrated to remove excess methylene chloride and unreacted acetyl chloride, leaving a white powder as the product. The crude product was recrystallized from methyl isobutyl ketone, resulting in 20.16 g of DAAMS as a white crystalline solid having a melting point of 126°C.

The polymerization was run in a 250 mL single-neck, round-bottom flask, fitted with a two-neck adapter upon which were mounted a glass paddle stirrer and a 13 cm Vigreux distillation column, distillation head with a thermometer, condenser and a receiver. Terephthalic acid (0.084 mol, 13.99 g) and DAAMS (0.084 mol, 26.12 g) were added to the reaction flask. The apparatus was evacuated and refilled with nitrogen three times. The flask was then immersed in a molten salt bath preheated to 260°C. The white suspension became a slurry over the next 2 hours as the temperature was slowly raised to 360°C. The pressure was

slowly lowered to 2×10^{-3} atmospheres. After an additional 30 minutes, the apparatus was cooled, and the vacuum was released under nitrogen. The isolated amount of opaque, pale yellow polyester was 26 g. The receiver contained 9.7 mL of acetic acid. The polyester was ground to a powder and was found to be insoluble in pentafluorophenol at 0.1 g/dL and 45°C.

- 5 DSC analysis of the polymer resulted in no observable endotherms or exotherms in the analysis range of 25°C to 400°C.

Example 12 - Preparation of Copolyester from DAAMS, Isophthalic Acid, 4-Acetoxybenzoic Acid (ABA), and 2,6-Naphthalenedicarboxylic Acid (NDCA)

- The polymerization was run in a 250 mL single-neck, round-bottom flask, fitted
10 with a two-neck adapter upon which were mounted a glass paddle stirrer and a 13 cm Vigreux distillation column, distillation head with a thermometer, condenser and a receiver. ABA (0.102 mol, 18.232 g), isophthalic acid (0.0169 mol, 2.80 g), NDCA (0.017 mol, 3.65 g), and DAAMS (0.034 mol, 10.46 g) were added to the reaction flask. The apparatus was evacuated and refilled with nitrogen three times. The flask was immersed in a molten salt bath preheated
15 to 260°C. When the solid reactant melt to form a molten reaction mass, stirring was started and lithium hydroxide (0.36 mL of 0.06 M aqueous solution) was added. The reaction temperature was raised to 340°C over a period of 2 hours at atmospheric pressure. Then the pressure was lowered to 2×10^{-3} atmospheres and this pressure was maintained for an additional hour at 340°C. After an additional 5 minutes, the reaction mass formed a ball on the stirrer shaft. The
20 vacuum was then released under nitrogen and the reaction vessel was removed from the salt bath. The reaction apparatus was cooled and disassembled. The volume of acetic acid recovered was 9.67 mL. The flask was broken away from the opaque yellow copolyester plug. The plug was sawed into chunks and then ground in a Wiley mill. DSC analysis, conducted at a scan rate of 10°C/minute, showed a melting transition at 280°C.

- 25 **Example 13 - Preparation of Polycarbonate of 4,4'-Dihydroxy- α,α' -diethylstilbene (DES)**

- This polycarbonate was prepared according to the general procedure of Example 1 using DES (0.14 mol, 36.5 g) and diphenyl carbonate (0.15 mol, 32.1 g). During the synthesis, conducted from 220 to 290°C, the reaction mixture remained isotropic. Phenol (25 g) was
30 removed as a distillate during the synthesis. The isolated yield of DES polycarbonate is 37 g. This polycarbonate had an IV of 0.37 dL/g (determined in chloroform at 25°C). DSC analysis showed a T_g at 87°C and no indications of a melting transition in the scan range of 25°C to 300°C. The polycarbonate was annealed at 125°C for 12 hours under an atmosphere of nitrogen. DSC analysis of the annealed sample showed a T_g at 92°C, but no evidence of melting
35 transitions.

Example 14 - Preparation of DHAMS/DES (90/10 Molar Ratio) Copolycarbonate

This copolycarbonate was prepared according to the general procedure of Example 1 using DES (0.016 mol, 4.19 g), DHAMS (0.14 mol, 31.76 g), and diphenyl carbonate

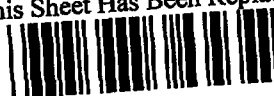
(0.16 mol, 33.41 g). During the synthesis, conducted from 220°C to 290°C, the reaction changed from an isotropic liquid to an opaque molten state at 270°C. Phenol (29 g) was removed as distillate during the synthesis. The resulting copolycarbonate was obtained as a white crystalline solid in an isolated yield of 35 g. DSC analysis showed a T_g at 87°C and a melting transition at 237°C during the heating scan and a crystallization exotherm at 112°C during the cooling scan. The polymer was insoluble in methylene chloride and chloroform at 0.1 g/dL. The polymer melt was optically anisotropic as determined by optical microscopy analysis described above.

Example 15 - Preparation of DHAMS/4,4'-Dihydroxystilbene (DHS) Copolycarbonate

DHAMS/DHS (90/10 molar ratio) copolycarbonate was prepared according to the general procedure of Example 1 using DHS (0.02 mol, 3.35 g), DHAMS (0.14 mol, 32.5 g), and diphenyl carbonate (0.16 mol, 34.2 g). DHS was prepared according to the procedure of McMurry and Silvestri, *J. Org. Chem.*, Vol. 40, p. 2687 (1975). The polymerization was conducted from 220°C to 290°C. The reaction mixture became opaque at 280°C. Phenol (30 g) was removed as a distillate during the synthesis. The resulting copolycarbonate, 37 g, was isolated as a white fibrous solid. The polymer was insoluble in methylene chloride or chloroform at 0.1 g/dL. DSC analysis showed a sharp melting transition at 283°C and a crystallization exotherm at 200°C during the first heating and cooling scans. The second heating and cooling scans of the sample showed a melting transition at 283°C and a crystallization exotherm at 196°C. The melt was optically anisotropic as determined by the methods described above.

Example 16 - Preparation of DHAMS/DHS (75/25 Molar Ratio) Copolycarbonate

This copolycarbonate was prepared according to the general procedure of Example 1 using DHS (0.04 mol, 8.45 g), DHAMS (0.121 mol, 27.3 g), and diphenyl carbonate (0.16 mol, 34.5 g). The reaction was conducted from 220°C to 320°C and the reaction mixture became opaque at 285°C. Phenol (30 g) was removed as a distillate during the synthesis. The resulting copolycarbonate, 35 g, was isolated as a white fibrous solid. The polymer was insoluble in methylene chloride or chloroform at 0.1 g/dL. DSC analysis showed a sharp melting transition at 299°C and a crystallization exotherm at 228°C. The melt was optically anisotropic as determined by the methods described above.



1. A polycarbonate, polyester, or polyestercarbonate composition prepared from a reaction mixture comprising at least one diol and at least one carbonate precursor or ester precursor, wherein

(a) at least 95 mole percent of the carbonate precursor or ester precursor present in the reaction mixture is selected from

(i) dialkyl carbonates, diarylcarbonates, carbonyl halides, and bis(trihaloalkyl) carbonates;

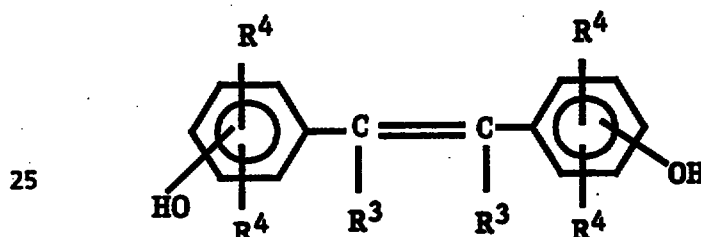
(ii) aromatic dicarboxylic acids, hydroxybenzoic acids, hydroxynaphthoic acids, hydroxybiphenyl acids, hydroxycinnamic acids, or the halides or metal salts of such acids; or

(iii) oligomers or polymers of (i) or (ii) containing carbonate or ester groups, which are prepared by contacting an excess over stoichiometry of at least one compound selected from (i) or (ii) with at least one monol or diol under reaction conditions sufficient to form the corresponding oligomer or polymer; or

(b) at least 95 mole percent of the diol present in the reaction mixture consists of one or more aromatic diols, at least 10 mole percent of which consists of one or more stilbene diols.

2. The composition of Claim 1 which comprises at least one thermotropic liquid crystalline polymer.

3. The composition of Claim 1 wherein the stilbene diol is of the following formula:



wherein R^3 independently in each occurrence is hydrogen, C_{1-8} alkyl, chlorine, bromine, or cyano; R^4 independently in each occurrence is hydrogen, halogen, alkyl, aryl, alkoxy, aryloxy, cyano, nitro, carboxamide, carboximide, or $R^5-C(O)-$, wherein R^5 is C_{1-8} alkyl or aryloxy.

4. The composition of Claim 3 wherein the stilbene diol is 4,4'-dihydroxystilbene; 4,4'-dihydroxy- α -methylstilbene; 4,4'-dihydroxy- α,α' -diethylstilbene; or 4,4'-dihydroxy- α,α' -dimethylstilbene.

5. The composition of Claim 1 wherein the reaction mixture contains 9,9-bis(4-hydroxyphenyl)fluorene, hydroquinone, 4,4'-dihydroxybiphenyl, or 4,4'-thiodiphenol.

6. The composition of Claim 1 wherein the reaction mixture contains bisphenol A.



7. The composition of Claim 1 wherein at least 25 mole percent of the aromatic diols present in the reaction mixture are stilbene diols.

8. The composition of Claim 1 wherein at least 50 mole percent of the aromatic diols present in the reaction mixture are stilbene diols.

5 9. The composition of Claim 1 wherein 100 mole percent of the aromatic diols present in the reaction mixture are stilbene diols.

10. The composition of Claim 1 wherein the polymers therein have a weight average molecular weight of at least 10,000.

10 11. The composition of Claim 2 wherein the difference between the clearing temperature and melt temperature is at least 50°C.

12. The composition of Claim 2 which has a melt temperature of at least 200°C.

13. A composition comprising at least one percent by weight of the polycarbonate, polyester, or polyestercarbonate composition of Claim 1 and at least one percent by weight of a different thermoplastic polymer.

15 14. A molded or extruded article comprising the compositions of Claim 1.

15. A polycarbonate prepared by reacting an excess over stoichiometry of diphenyl carbonate with a stilbene diol.

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