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| <p>(54) Title: THERMALLY STABLE POLYMERS, METHOD OF PREPARATION, AND ARTICLES MADE THEREFROM</p> | | |
| <p>(57) Abstract</p> <p>Thermally stable polymers comprising resorcinol arylate chain members are prepared using an interfacial method comprising the steps of: (a) combining at least one resorcinol moiety and at least one catalyst in a mixture of water and at least one organic solvent substantially immiscible with water; and (b) adding to the mixture from (a) at least one dicarboxylic acid dichloride while maintaining the pH between 3 and 8.5 through the presence of an acid acceptor, wherein the total molar amount of acid chloride groups is stoichiometrically deficient relative to the total molar amount of phenolic groups.</p> | | |

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THERMALLY STABLE POLYMERS, METHOD OF
PREPARATION, AND ARTICLES MADE
THEREFROM

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of U.S. Provisional Application No. 60/134,692, filed May 18, 1999.

BACKGROUND OF THE INVENTION

This invention relates to thermally stable polymers comprising resorcinol arylate polyester chain members, a method for their preparation, and multilayer articles made therefrom.

5 Various polymeric articles have a problem of long term color instability. In many cases this instability is seen as yellowing of the polymer, detracting from its attractiveness and also transparency when the polymer was initially transparent. Loss of gloss can also be an undesirable long term phenomenon.

10 Yellowing of polymers is often caused by the action of ultraviolet radiation, and such yellowing is frequently designated "photoyellowing". Numerous means for suppressing photoyellowing have been employed and proposed. Many of these involve incorporation in the polymer of ultraviolet absorbing compounds (UVA's). For the most part, UVA's are low molecular weight compounds, which must be employed at relatively low levels, typically up to 1% by weight, to avoid degradation of the physical properties of the polymer such as impact strength and high
15 temperature properties as reflected in heat distortion temperature. Another problem of concern with polymers such as aromatic polycarbonates and addition polymers of alkenylaromatic compounds such as styrene is susceptibility to attack by organic liquids.

20 One way of protecting a resinous article against photoyellowing and loss of gloss is to apply a coating of a weatherable second polymer, the term "weatherable" as used herein signifying resistance to such phenomena. Coatings made from polyesters containing resorcinol arylate units often possess good weatherability properties. The arylate moieties typically contain isophthalate, terephthalate, and

especially mixtures of iso- and terephthalate units. Polyesters of resorcinol with mixtures of isophthalate and terephthalate chain members typically have good weatherability properties and may provide protection against photoyellowing when coated over a resinous substrate.

5 The good weatherability properties of polyesters containing resorcinol arylate units is believed to arise in large part from the screening effect said polymers may provide to ultraviolet (UV) light. On exposure to UV light polymers comprising resorcinol arylate chain members may undergo photochemical Fries rearrangement converting at least a portion of the polymer from polyester chain members to
10 o-hydroxybenzophenone-type chain members. The o-hydroxybenzophenone-type chain members act to screen further UV light and protect UV-sensitive components in a resorcinol arylate-containing composition. The good weatherability properties of polymers comprising resorcinol arylate chain members make them especially useful in blends and in multilayer articles in which said polymers may act as a protecting
15 layer for more sensitive substrate components.

Copolyesters comprising resorcinol iso- and terephthalate polyester chain members in combination with diacid or diol alkylene chain members (so-called "soft-block" chain members) are disclosed in commonly owned, co-pending application serial number 09/030,076. These copolymers have excellent weatherability and
20 flexibility. Copolyestercarbonates comprising resorcinol iso- and terephthalate polyester chain members in combination with carbonate chain members are disclosed in commonly owned, co-pending application serial number 09/181,902. These copolymers have excellent weatherability and are compatible with polycarbonates in blends.

25 Polyesters containing resorcinol arylate chain members have been prepared by melt methods as disclosed in U.S. Patent No. 4,127,560 and in Japanese Kokai 1/201,326. The methods may provide polyesters containing isophthalate and terephthalate chain members but do not allow the incorporation of greater than 30 mole % terephthalate. In addition, the polyesters obtained have unacceptable color.

30 Polyesters containing resorcinol arylate chain members have also been prepared by an interfacial method. The interfacial method comprises a solvent mixture containing water and at least one organic solvent substantially immiscible with water. According to U.S. Patent No. 3,460,961 and Eareckson, Journal of Polymer Science, vol. XL, pp. 399-406 (1959), preparation of resorcinol arylate

polyesters with a mixture of iso- and terephthalate chain members is performed by an interfacial method in water and a water-immiscible solvent such as chloroform or dichloromethane using 1:1 stoichiometric ratio of resorcinol to either iso- or terephthaloyl dichloride, or a mixture thereof, in the presence of aqueous sodium hydroxide. The resorcinol is combined with the aqueous sodium hydroxide before addition of acid chlorides, and the reaction is run at pH which is initially high but which decreases as the reaction proceeds. The molecular weight of the polymers is not controlled. The method provides polymer with very high weight average molecular weight (Mw), making the polymer unsuitable for some applications. Furthermore, the polymer has poor thermal stability and loses molecular weight upon thermal treatment.

Multilayer articles containing layers made from resorcinol arylate-containing polyester have been described by Cohen et al., *Journal of Polymer Science : Part A-1*, vol. 9, 3263-3299 (1971) and in U.S. Patent No. 3,460,961. The polyester was made either in solution or by an interfacial process. The solution method requires the use of a stoichiometric amount of an organic base, such as a tertiary amine, which must be isolated and recovered for reuse in any economical, environmentally friendly process. Both methods produce thermally unstable polyester which can only be applied by solution coating followed by evaporation of the solvent to make a multilayer article. This solution coating method has numerous deficiencies, some of which are mentioned in the Cohen et al. paper at page 3267: namely, the necessity to use high priced and toxic solvents, the inherently low concentration of the arylate polymer in the solvent and the tendency of the solutions to gel. Accordingly, the described polyesters were considered "unacceptable coating candidates".

Japanese Kokai 1/199,841 discloses articles having a substrate layer comprising at least 90 mole percent poly(ethylene terephthalate) and a gas barrier coating layer which is a polyester of resorcinol and a minimum of 50 mole % isophthalic acid, optionally with copolyester units derived from another dicarboxylic acid such as terephthalic acid, naphthalenedicarboxylic acid or various other specifically named dicarboxylic acids. The disclosed articles may be prepared by a series of operations including co-injection molding. However, the only types of articles disclosed are bottles, which are produced from a co-injection molded parison by subsequent blow molding. Larger articles, such as external automobile body parts, are not disclosed and no method for their production is suggested, nor are articles in which the substrate layer is anything other than poly(ethylene terephthalate). In

addition, the resorcinol isophthalate polyesters were prepared either by melt methods which do not allow the incorporation of greater than 30 mole % terephthalate and give polyester with unacceptable color, or by the interfacial method which produces thermally unstable polyester.

- 5 It remains of interest, therefore, to develop a method for preparing weatherable, solvent resistant multilayer articles which are capable of use for such varied purposes as body parts for outdoor vehicles and devices such as automobiles. There is also a particular need for polymers comprising resorcinol arylate chain members having controlled molecular weight, high thermal stability, and low color.
- 10 There is also a particular need for polymers comprising resorcinol arylate chain members that can be processed using typical melt processing techniques.

BRIEF SUMMARY OF THE INVENTION

The present inventors have identified the primary source of poor thermal stability in polymers comprising resorcinol arylate polyester chain members prepared by the interfacial method, and have discovered a method to prepare said polymers in thermally stable form with controlled molecular weight. The new method also allows the preparation of virtually colorless polymers comprising resorcinol arylate polyester chain members.

15

In one of its aspects the present invention provides an interfacial method for preparing polymers comprising resorcinol arylate polyester chain members substantially free of anhydride linkages linking at least two mers of the polymer chain, comprising the steps of :

20

(a) combining at least one resorcinol moiety and at least one catalyst in a mixture of water and at least one organic solvent substantially immiscible with water; and

25 (b) adding to the mixture from (a) at least one dicarboxylic acid dichloride while maintaining the pH between 3 and 8.5 through the presence of an acid acceptor, wherein the total molar amount of acid chloride groups is stoichiometrically deficient relative to the total molar amount of phenolic groups.

In another of its aspects the invention provides a polymer consisting essentially of resorcinol arylate polyester chain members substantially free of

30

anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method comprising the above steps.

In yet another of its aspects the invention provides a copolymer consisting essentially of resorcinol arylate polyester chain members in combination with C₃₋₂₀ straight chain alkylene, C₃₋₁₀ branched alkylene, or C₄₋₁₀ cyclo- or bicycloalkylene chain members, substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method comprising the above steps.

In still another of its aspects the invention provides a copolymer consisting essentially of resorcinol arylate polyester chain members in combination with organic carbonate chain members, substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method, comprising the above steps.

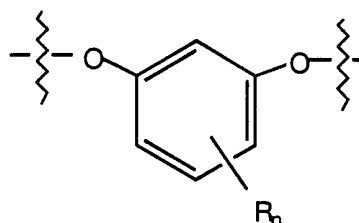
DETAILED DESCRIPTION OF THE INVENTION

In one embodiment the present invention comprises an interfacial method for preparing thermally stable polymers comprising resorcinol arylate polyester chain members which derive their thermal stability in large part from being substantially free of anhydride linkages in the polymer chains. In another embodiment the present invention comprises the thermally stable polymers prepared by such an interfacial method.

Thermal stability within the context of the present invention refers to resistance of a polymer to molecular weight degradation under thermal conditions. Thus, a polymer with poor thermal stability shows significant molecular weight degradation under thermal conditions, such as during extrusion, molding, thermoforming, hot-pressing, and like conditions. Molecular weight degradation may also be manifest through color formation and/or in the degradation of other properties such as weatherability, gloss, mechanical properties, and/or thermal properties. Molecular weight degradation can also cause significant variation in processing conditions as the melt viscosity changes.

In one of its aspects the method of the present invention provides thermally stable polymers comprising arylate polyester chain members. Said chain members comprise at least one diphenol residue in combination with at least one aromatic dicarboxylic acid residue. The preferred diphenol residue, illustrated in Formula I, is

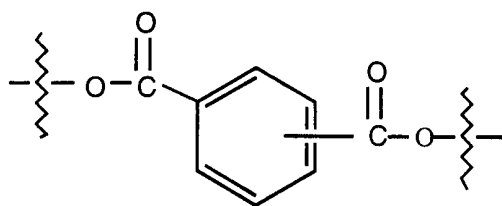
derived from a 1,3-dihydroxybenzene moiety, commonly referred to throughout this specification as resorcinol or resorcinol moiety. Resorcinol or resorcinol moiety as used within the context of the present invention should be understood to include both unsubstituted 1,3-dihydroxybenzene and substituted 1,3-dihydroxybenzenes unless explicitly stated otherwise.



Formula I

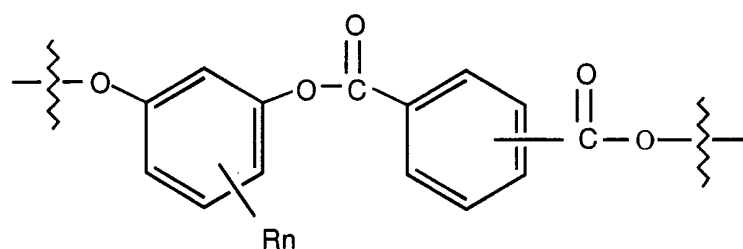
In Formula I R is at least one of C₁₋₁₂ alkyl or halogen, and n is 0-3.

Suitable dicarboxylic acid residues include aromatic dicarboxylic acid residues derived from monocyclic moieties, preferably isophthalic acid, terephthalic acid, or mixtures of isophthalic and terephthalic acids, or from polycyclic moieties, including diphenyl dicarboxylic acid, diphenylether dicarboxylic acid, and naphthalenedicarboxylic acid, preferably naphthalene-2,6-dicarboxylic acid. Preferably, the aromatic dicarboxylic acid residues are derived from mixtures of isophthalic and/or terephthalic acids as typically illustrated in Formula II.



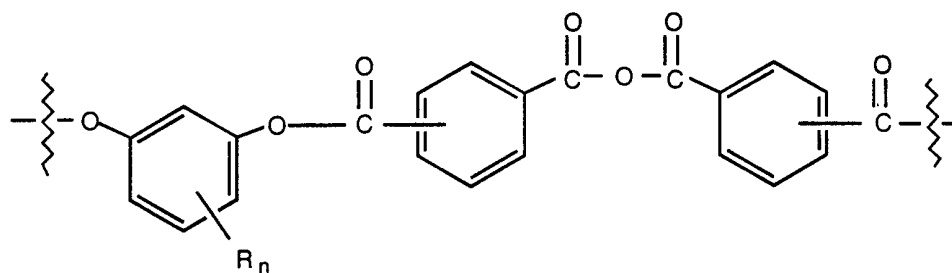
Formula II

Therefore, in one embodiment the present invention provides thermally stable polymers comprising resorcinol arylate polyester chain members as typically illustrated in Formula III wherein R and n are as previously defined :



Formula III

Previous interfacial methods for preparing polyesters comprising resorcinol
 arylate chain members typically provide polymers with poor thermal stability and
 5 uncontrolled molecular weight. The present inventors have discovered that a primary
 reason for poor thermal stability is the presence of anhydride linkages in the
 backbone of the polyester chain. Typical anhydride linkages are illustrated in Formula
 IV. Such anhydride linkages link at least two mers in a polymer chain and may arise
 through combination of two isophthalate or terephthalate moieties or mixtures
 10 thereof, although it is to be understood that anhydride linkages in polymers
 comprising resorcinol arylate chain members may arise through combination of any
 suitable similar dicarboxylic acid residues or mixtures of suitable dissimilar
 dicarboxylic acid residues present in a reaction mixture.



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Formula IV

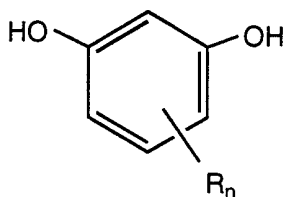
Although the invention is not limited by theory, it is believed that the
 anhydride linkage represents a weak bond in the polyester chain, which can break
 under thermal processing conditions to produce shorter chains terminated by acid
 20 end-groups. These acid end-groups, in turn, may accelerate the hydrolysis of the
 arylate moiety, generating additional carboxyl and hydroxyl end-groups, and further
 contributing to the molecular weight degradation, and loss in other desirable
 properties. Anhydride linkages may arise through several mechanisms. In one

mechanism a carboxylic acid chloride may be hydrolyzed to carboxylic acid when the esterification reaction is run at high pH. The carboxylic acid or corresponding carboxylate may then react with another carboxylic acid chloride to yield an anhydride linkage.

5 Anhydride linkages may be detected by means known to those skilled in the art such as by ^{13}C nuclear magnetic resonance spectroscopy (NMR). For example, resorcinol arylate polyesters comprising dicarboxylic acid residues derived from a mixture of iso- and terephthalic acids typically show ^{13}C NMR resonances attributed to anhydride at 161.0 and 161.1 ppm (in deuteriochloroform relative to
10 tetramethylsilane), as well as resonances for the polymer carboxylic acid and hydroxyl end-groups. After thermal processing (for example, extrusion and/or molding), the polymer molecular weight decreases, and the anhydride resonances typically decrease, while those of the acid and hydroxyl end-groups typically increase.

15 Anhydride linkages in polymers comprising resorcinol arylate polyester chain members may also be detected by reaction of polymer with a nucleophile, such as a secondary amine. For example, resorcinol arylate polyesters comprising dicarboxylic acid residues derived from a mixture of iso- and terephthalic acids can be dissolved in a convenient solvent, such as dichloromethane, and treated with a secondary amine,
20 such as dibutylamine or diisobutylamine, for several minutes at ambient temperature. Comparison of the starting polymer molecular weight to that after amine treatment typically shows a decrease in molecular weight which can be correlated with the corresponding decrease observed under typical thermal processing conditions. Although the invention is not meant to be limited by theory, it is believed that
25 nucleophiles, such as secondary amine and phenolic, attack anhydride linkages (as opposed to ester linkages) selectively under the reaction conditions. The decrease in molecular weight upon reaction with amine nucleophile is therefore an indication of the presence of anhydride functionality in the polymer.

30 In one of its aspects the present invention provides an interfacial method for preparing polymers comprising resorcinol arylate polyester chain members substantially free of anhydride linkages, said method comprising a first step of combining at least one resorcinol moiety and at least one catalyst in a mixture of water and at least one organic solvent substantially immiscible with water. Suitable resorcinol moieties comprise units of Formula V :



Formula V

wherein R is at least one of C₁₋₁₂ alkyl or halogen, and n is 0-3. Alkyl groups, if
 5 present, are preferably straight-chain or branched alkyl groups, and are most often
 located in the ortho position to both oxygen atoms although other ring locations are
 contemplated. Suitable C₁₋₁₂ alkyl groups include methyl, ethyl, n-propyl, isopropyl,
 butyl, iso-butyl, t-butyl, nonyl, decyl, and aryl-substituted alkyl, including benzyl,
 with methyl being particularly preferred. Suitable halogen groups are bromo, chloro,
 10 and fluoro. The value for n may be 0-3, preferably 0-2, and more preferably 0-1. A
 preferred resorcinol moiety is 2-methylresorcinol. The most preferred resorcinol
 moiety is an unsubstituted resorcinol moiety in which n is zero.

The method further comprises combining at least one catalyst with the
 reaction mixture. Said catalyst may be present at a total level of 0.1 to 10 mole %, and
 15 preferably 0.2 to 6 mole % based on total molar amount of acid chloride groups.
 Suitable catalysts comprise tertiary amines, quaternary ammonium salts, quaternary
 phosphonium salts, hexaalkylguanidinium salts, and mixtures thereof. Suitable
 tertiary amines include triethylamine, dimethylbutylamine, diisopropylethylamine,
 2,2,6,6-tetramethylpiperidine, and mixtures thereof. Other contemplated tertiary
 20 amines include N-C₁-C₆-alkyl-pyrrolidines, such as N-ethylpyrrolidine, N-C₁-C₆-
 piperidines, such as N-ethylpiperidine, N-methylpiperidine, and N-
 isopropylpiperidine, N-C₁-C₆-morpholines, such as N-ethylmorpholine and N-
 isopropyl-morpholine, N-C₁-C₆-dihydroindoles, N-C₁-C₆-dihydroisoindoles, N-C₁-
 C₆-tetrahydroquinolines, N-C₁-C₆-tetrahydroisoquinolines, N-C₁-C₆-benzo-
 25 morpholines, 1-azabicyclo-[3.3.0]-octane, quinuclidine, N-C₁-C₆-alkyl-2-azabicyclo-
 [2.2.1]-octanes, N-C₁-C₆-alkyl-2-azabicyclo-[3.3.1]-nonanes, and N-C₁-C₆-alkyl-3-
 azabicyclo-[3.3.1]-nonanes, N,N,N',N'-tetraalkylalkylene-diamines, including
 N,N,N',N'-tetraethyl-1,6-hexanediamine. Particularly preferred tertiary amines are
 triethylamine and N-ethylpiperidine.

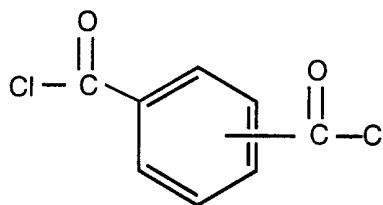
When the catalyst consists of at least one tertiary amine alone, then said catalyst may be present at a total level of 0.1 to 10 mole %, preferably 0.2 to 6 mole %, more preferably 1 to 4 mole %, and most preferably 2.5 to 4 mole % based on total molar amount of acid chloride groups. In one embodiment of the invention all of
5 the at least one tertiary amine is present at the beginning of the reaction before addition of dicarboxylic acid dichloride to resorcinol moiety. In another embodiment a portion of any tertiary amine is present at the beginning of the reaction and a portion is added following or during addition of dicarboxylic acid dichloride to resorcinol moiety. In this latter embodiment the amount of any tertiary amine initially present
10 with resorcinol moiety may range from about 0.005 wt.% to about 10 wt.%, preferably from about 0.01 to about 1 wt.%, and more preferably from about 0.02 to about 0.3 wt.% based on total amine.

Suitable quaternary ammonium salts, quaternary phosphonium salts, and
15 hexaalkylguanidinium salts include halide salts such as tetraethylammonium bromide, tetraethylammonium chloride, tetrapropylammonium bromide, tetrapropylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium chloride, methyltributylammonium chloride, benzyltributylammonium chloride, benzyltriethylammonium chloride, benzyltrimethylammonium chloride, trioctylmethylammonium chloride, cetyltrimethylbenzylammonium chloride,
20 octyltriethylammonium bromide, decyltriethylammonium bromide, lauryltriethylammonium bromide, cetyltrimethylammonium bromide, cetyltriethylammonium bromide, N-laurylpyridinium chloride, N-laurylpyridinium bromide, N-heptylpyridinium bromide, tricapylylmethylammonium chloride (sometimes known as ALIQUAT 336), methyltri-C₈-C₁₀-alkyl-ammonium chloride
25 (sometimes known as ADOGEN 464), N,N,N',N',N'-pentaalkyl-alpha, omega-amineammonium salts such as disclosed in U.S. Patent 5,821,322; tetrabutylphosphonium bromide, benzyltriphenylphosphonium chloride, triethyloctadecylphosphonium bromide, tetraphenylphosphonium bromide, triphenylmethylphosphonium bromide, trioctylethylphosphonium bromide,
30 cetyltriethylphosphonium bromide, hexaalkylguanidinium halides, hexaethylguanidinium chloride, and the like, and mixtures thereof.

Organic solvents substantially immiscible with water include those which are less than about 5 wt.%, and preferably less than about 2 wt.% soluble in water under the reaction conditions. Suitable organic solvents include dichloromethane,
35 trichloroethylene, tetrachloroethane, chloroform, 1,2-dichloroethane, toluene, xylene,

trimethylbenzene, chlorobenzene, o-dichlorobenzene, and mixtures thereof. An especially preferred solvent is dichloromethane.

Suitable dicarboxylic acid dichlorides comprise aromatic dicarboxylic acid dichlorides derived from monocyclic moieties, preferably isophthaloyl dichloride, terephthaloyl dichloride, or mixtures of isophthaloyl and terephthaloyl dichlorides, or from polycyclic moieties, including diphenyl dicarboxylic acid dichloride, diphenylether dicarboxylic acid dichloride, and naphthalenedicarboxylic acid dichloride, preferably naphthalene-2,6-dicarboxylic acid dichloride; or from mixtures of monocyclic and polycyclic aromatic dicarboxylic acid dichlorides. Preferably, the dicarboxylic acid dichloride comprises mixtures of isophthaloyl and/or terephthaloyl dichlorides as typically illustrated in Formula VI.



Formula VI

Either or both of isophthaloyl and terephthaloyl dichlorides may be present. In especially preferred embodiments the dicarboxylic acid dichlorides comprise mixtures of isophthaloyl and terephthaloyl dichloride in a molar ratio of isophthaloyl to terephthaloyl of about 0.25-4.0:1, preferably about 0.4-2.5:1, and more preferably about 0.67-1.5:1.

The pH of the reaction mixture is maintained between about 3 and about 8.5, and preferably between about 5 and about 8, throughout addition of the at least one dicarboxylic acid dichloride to the at least one resorcinol moiety. Suitable reagents to maintain the pH include alkali metal hydroxides, alkaline earth hydroxides, and alkaline earth oxides. Preferred reagents are potassium hydroxide and sodium hydroxide. A particularly preferred reagent is sodium hydroxide. The reagent to maintain pH may be included in the reaction mixture in any convenient form. Preferably, said reagent is added to the reaction mixture as an aqueous solution simultaneously with the at least one dicarboxylic acid dichloride.

The temperature of the reaction mixture may be any convenient temperature that provides a rapid reaction rate and a resorcinol arylate-containing polymer

substantially free of anhydride linkages. Convenient temperatures include those from about -20°C to the boiling point of the water-organic solvent mixture under the reaction conditions. In a preferred embodiment the reaction is performed at the boiling point of the organic solvent in the water-organic solvent mixture. In an especially preferred embodiment the reaction is performed at the boiling point of dichloromethane.

The total molar amount of acid chloride groups added to the reaction mixture is stoichiometrically deficient relative to the total molar amount of phenolic groups. Said stoichiometric ratio is desirable so that hydrolysis of acid chloride groups is minimized, and so that nucleophiles such as phenolic and/or phenoxide may be present to destroy any adventitious anhydride linkages, should any form under the reaction conditions. The total molar amount of acid chloride groups includes the at least one dicarboxylic acid dichloride, and any mono-carboxylic acid chloride chain-stoppers and any tri- or tetra-carboxylic acid tri- or tetra-chloride branching agents which may be used. The total molar amount of phenolic groups includes resorcinol moieties, and any mono-phenolic chain-stoppers and any tri- or tetra-phenolic branching agents which may be used. The stoichiometric ratio of total phenolic groups to total acid chloride groups is preferably about 1.5-1.01 : 1 and more preferably about 1.2-1.02 : 1.

The presence or absence of adventitious anhydride linkages following complete addition of the at least one dicarboxylic acid dichloride to the at least one resorcinol moiety will typically depend upon the exact stoichiometric ratio of reactants and the amount of catalyst present, as well as other variables. For example, if a sufficient molar excess of total phenolic groups is present, anhydride linkages are often found to be absent. Often a molar excess of at least about 1% and preferably at least about 3% of total amount of phenolic groups over total amount of acid chloride groups may suffice to eliminate anhydride linkages under the reaction conditions. When anhydride linkages may be present, it is often desirable that the final pH be greater than 7 so that nucleophiles such as phenolic, phenoxide and/or hydroxide may be present to destroy any adventitious anhydride linkages. Therefore, in one of its aspects the method of the invention may further comprise the step of adjusting the pH of the reaction mixture to between 7 and 12, preferably to between 8 and 12, and more preferably to between 8.5 and 12, following complete addition of the at least one dicarboxylic acid dichloride to the at least one resorcinol moiety. The pH may be

adjusted by any convenient method, preferably using an aqueous base such as aqueous sodium hydroxide.

5 Provided the final pH of the reaction mixture is greater than 7, the method of the invention may further comprise the step of stirring the reaction mixture for a time sufficient to destroy completely any adventitious anhydride linkages, should any be present. The necessary stirring time will depend upon reactor configuration, stirrer geometry, stirring rate, temperature, total solvent volume, organic solvent volume, anhydride concentration, pH, and other factors. In some instances the necessary stirring time is essentially instantaneous, for example within seconds of pH adjustment to above 7, assuming any adventitious anhydride linkages were present to begin with. For typical laboratory scale reaction equipment a stirring time of at least about 3 minutes, and preferably at least about 5 minutes may be required. By this process nucleophiles, such as phenolic, phenoxide and/or hydroxide, may have time to destroy completely any adventitious anhydride linkages, should any be present.

15 At least one chain-stopper (also referred to sometimes hereinafter as capping agent) may also be present in the method and compositions of the invention. A purpose of adding at least one chain-stopper is to limit the molecular weight of polymer comprising resorcinol arylate polyester chain members, thus providing polymer with controlled molecular weight and favorable processability. Typically, at least one chain-stopper is added when the resorcinol arylate-containing polymer is not required to have reactive end-groups for further application. In the absence of chain-stopper resorcinol arylate-containing polymer may be either used in solution or recovered from solution for subsequent use such as in copolymer formation which may require the presence of reactive end-groups, typically hydroxy, on the resorcinol-arylate polyester segments. A chain-stopper may be at least one of mono-phenolic compounds, mono-carboxylic acid chlorides, and/or mono-chloroformates. Typically, the at least one chain-stopper may be present in quantities of 0.05 to 10 mole %, based on resorcinol moieties in the case of mono-phenolic compounds and based on acid dichlorides in the case mono-carboxylic acid chlorides and/or mono-chloroformates.

Suitable mono-phenolic compounds include monocyclic phenols, such as phenol, C₁-C₂₂ alkyl-substituted phenols, p-cumyl-phenol, p-tertiary-butyl phenol, hydroxy diphenyl; monoethers of diphenols, such as p-methoxyphenol. Alkyl-substituted phenols include those with branched chain alkyl substituents having 8 to 9

carbon atoms, preferably in which about 47 to 89% of the hydrogen atoms are part of methyl groups as described in U.S. Patent 4,334,053. For some embodiments the use of a mono-phenolic UV screener as capping agent is preferred. Such compounds include 4-substituted-2-hydroxybenzophenones and their derivatives, aryl salicylates, 5 monoesters of diphenols, such as resorcinol monobenzoate, 2-(2-hydroxyaryl)-benzotriazoles and their derivatives, 2-(2-hydroxyaryl)-1,3,5-triazines and their derivatives, and like compounds. Especially preferred mono-phenolic chain-stoppers are phenol, p-cumylphenol, and resorcinol monobenzoate.

Suitable mono-carboxylic acid chlorides include monocyclic, mono-10 carboxylic acid chlorides, such as benzoyl chloride, C₁-C₂₂ alkyl-substituted benzoyl chloride, toluoyl chloride, halogen-substituted benzoyl chloride, bromobenzoyl chloride, cinnamoyl chloride, 4-nadimidobenzoyl chloride, and mixtures thereof; polycyclic, mono-carboxylic acid chlorides, such as trimellitic anhydride chloride, and naphthoyl chloride; and mixtures of monocyclic and polycyclic mono-carboxylic 15 acid chlorides. The chlorides of aliphatic monocarboxylic acids with up to 22 carbon atoms are also suitable. Functionalized chlorides of aliphatic monocarboxylic acids, such as acryloyl chloride and methacryoyl chloride, are also suitable. Suitable mono-chloroformates include monocyclic, mono-chloroformates, such as phenyl chloroformate, alkyl-substituted phenyl chloroformate, p-cumyl phenyl 20 chloroformate, toluene chloroformate, and mixtures thereof.

A chain-stopper can be combined together with the resorcinol moieties, can be contained in the solution of dicarboxylic acid dichlorides, or can be added to the reaction mixture after production of a precondensate. If mono-carboxylic acid chlorides and/or mono-chloroformates are used as chain-stoppers, they are preferably 25 introduced together with dicarboxylic acid dichlorides. These chain-stoppers can also be added to the reaction mixture at a moment when the chlorides of dicarboxylic acid have already reacted substantially or to completion. If phenolic compounds are used as chain-stoppers, they can be added to the reaction mixture during the reaction, or, more preferably, before the beginning of the reaction between resorcinol moiety and 30 acid chloride moiety. When hydroxy-terminated resorcinol arylate-containing precondensate or oligomers are prepared, then chain-stopper may be absent or only present in small amounts to aid control of oligomer molecular weight.

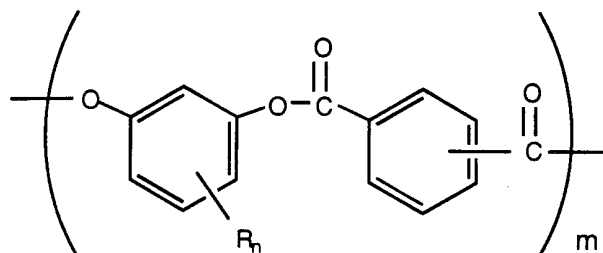
In another embodiment the invention may encompass the inclusion of at least one branching agent such as a trifunctional or higher functional carboxylic acid

chloride and/or trifunctional or higher functional phenol. Such branching agents, if included, can preferably be used in quantities of 0.005 to 1 mole %, based on dicarboxylic acid dichlorides or resorcinol moieties used, respectively. Suitable branching agents include, for example, trifunctional or higher carboxylic acid chlorides, such as trimesic acid trichloride, cyanuric acid trichloride, 3,3',4,4'-benzophenone tetracarboxylic acid tetrachloride, 1,4,5,8-naphthalene tetracarboxylic acid tetrachloride or pyromellitic acid tetrachloride, and trifunctional or higher phenols, such as phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-2-heptene, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane, 1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri-(4-hydroxyphenyl)-ethane, tri-(4-hydroxyphenyl)-phenyl methane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)-cyclohexyl]-propane, 2,4-bis-(4-hydroxyphenylisopropyl)-phenol, tetra-(4-hydroxyphenyl)-methane, 2,6-bis-(2-hydroxy-5-methylbenzyl)-4-methyl phenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane, tetra-(4-[4-hydroxyphenylisopropyl]-phenoxy)-methane, 1,4-bis-[(4,4-dihydroxytriphenyl)methyl]-benzene. Phenolic branching agents may be introduced first with the resorcinol moieties whilst acid chloride branching agents may be introduced together with acid dichlorides.

For some applications such as for copolymer formation the resorcinol arylate-containing polymer may remain in solution for subsequent process steps. In other instances such as in the production of resorcinol arylate polyester the polymer will normally be isolated from solution. Therefore, in another embodiment of the invention the resorcinol arylate-containing polymer is recovered from the reaction mixture. Recovery methods are well known to those skilled in the art and may include such steps as acidification of the mixture, for example with phosphorous acid; subjecting the mixture to liquid-liquid phase separation; washing the organic phase with water and/or a dilute acid such as hydrochloric acid or phosphoric acid; precipitating by usual methods such as through treatment with water or anti-solvent precipitation with, for example, methanol, ethanol, and/or isopropanol; isolating the resulting precipitates; and drying to remove residual solvents.

If desired, the resorcinol arylate polymers of the invention may be made by the present method further comprising the addition of a reducing agent. Suitable reducing agents include, for example, sodium sulfite, sodium gluconate, or a borohydride, such as sodium borohydride. When present, any reducing agents are typically used in quantities of from 0.25 to 2 mole %, based on moles of resorcinol moiety.

In one of its embodiments the invention comprises thermally stable resorcinol arylate polyesters made by the present method and substantially free of anhydride linkages linking at least two mers of the polyester chain. In a particular embodiment said polyesters comprise dicarboxylic acid residues derived from a mixture of iso- and terephthalic acids as illustrated in Formula VII:



Formula VII

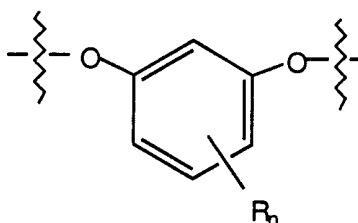
wherein R is at least one of C₁₋₁₂ alkyl or halogen, n is 0-3, and m is at least about 8. Preferably, n is zero and m is between about 10 and about 300. The molar ratio of isophthalate to terephthalate is about 0.25-4.0:1, preferably about 0.4-2.5:1, and more preferably about 0.67-1.5:1. Substantially free of anhydride linkages means that said polyesters show decrease in molecular weight of less than 30% and preferably less than 10% upon heating said polymer at a temperature of about 280-290°C for five minutes.

The present invention also encompasses thermally stable copolymers containing segments comprising resorcinol arylate polyester chain members made by the present method and substantially free of anhydride linkages linking at least two mers of the copolymer chain. Thus, in another of its embodiments the present invention comprises thermally stable copolyesters comprising resorcinol arylate polyester chain members in combination with dicarboxylic acid or diol alkylene chain members (so-called "soft-block" segments), said copolyesters being substantially free of anhydride linkages in the polyester segments. Substantially free of anhydride linkages means that the copolyesters show decrease in molecular weight of less than 10% and preferably less than 5% upon heating said copolyester at a temperature of about 280-290°C for five minutes. Related copolyesters containing soft-block segments are disclosed in commonly owned, co-pending application Serial No. 09/030,076, the disclosure of which is incorporated by reference herein.

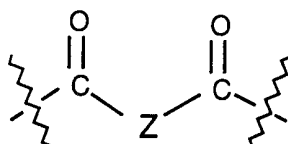
The term soft-block as used herein, indicates that some segments of the polymers are made from non-aromatic monomer units. Such non-aromatic monomer

units are generally aliphatic and are known to impart flexibility to the soft-block-containing polymers. The copolymers include those comprising structural units of Formulas I, VIII, and IX :

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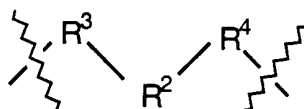


Formula I



Formula VIII

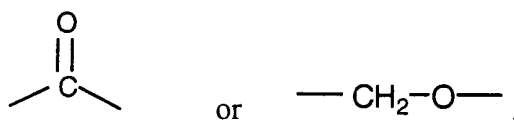
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Formula IX

wherein R and n are as previously defined, Z is a divalent aromatic radical, R² is a C₃₋₂₀ straight chain alkylene, C₃₋₁₀ branched alkylene, or C₄₋₁₀ cyclo- or bicycloalkylene group, and R³ and R⁴ each independently represent

15



wherein Formula IX contributes from about 1 to about 45 mole percent to the ester linkages of the polyester. Additional embodiments of the present invention provide a composition wherein Formula IX contributes from about 5 to about 40 mole percent to the ester linkages of the polyester, with about 5 to about 20 mole percent

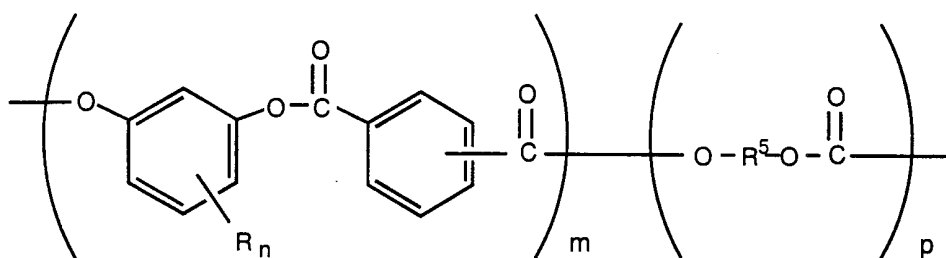
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being particularly preferred. Another embodiment provides a composition wherein R^2 represents C_{3-14} straight chain alkylene, or C_{5-6} cycloalkylene, with a preferred composition being one wherein R^2 represents C_{3-10} straight-chain alkylene or C_6 -cycloalkylene. Formula VIII represents an aromatic dicarboxylic acid residue. The
5 divalent aromatic radical Z in Formula VIII may be derived from at least one of the suitable dicarboxylic acid residues as defined hereinabove, and preferably at least one of 1,3-phenylene, 1,4-phenylene, or 2,6-naphthylene. In more preferred embodiments Z comprises at least about 40 mole percent 1,3-phenylene. In preferred embodiments of copolyesters containing soft-block chain members n in Formula I is zero.

10 Preferred copolyesters containing resorcinol arylate chain members are those comprising from about 1 to about 45 mole % sebacate or 1,4-dicarboxylate units. A particularly preferred copolyester containing resorcinol arylate chain members is one comprising resorcinol isophthalate and resorcinol sebacate units in molar ratio between 8.5:1.5 and 9.5:0.5. In a preferred procedure said preferred copolyester is
15 prepared using sebacyl chloride in combination with isophthaloyl chloride.

In another of its embodiments the present invention comprises thermally stable block copolyestercarbonates comprising resorcinol arylate-containing block segments in combination with organic carbonate block segments. The segments comprising resorcinol arylate chain members in such copolymers are substantially
20 free of anhydride linkages. Substantially free of anhydride linkages means that the copolyestercarbonates show decrease in molecular weight of less than 10% and preferably less than 5% upon heating said copolyestercarbonate at a temperature of about 280-290°C for five minutes. Related block copolyestercarbonates are disclosed in commonly owned, co-pending application Serial No. 09/181,902, the disclosure of
25 which is incorporated by reference herein.

The block copolyestercarbonates include those comprising alternating arylate and organic carbonate blocks, typically as illustrated in Formula X, wherein R and n are as previously defined, and R^5 is at least one divalent organic radical :



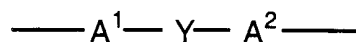
Formula X

The arylate blocks have a degree of polymerization (DP), represented by m , of at least about 4, preferably at least about 10, more preferably at least about 20 and most preferably about 30-150. The DP of the organic carbonate blocks, represented by p , is generally at least about 10, preferably at least about 20 and most preferably about 50-200. The distribution of the blocks may be such as to provide a copolymer having any desired weight proportion of arylate blocks in relation to carbonate blocks. In general, the content of arylate blocks is preferably about 10-95% by weight and more preferably about 50-95% by weight.

Although a mixture of iso- and terephthalate is illustrated in Formula X, the dicarboxylic acid residues in the arylate blocks may be derived from any suitable dicarboxylic acid residue, as defined hereinabove, or mixture of suitable dicarboxylic acid residues, including those derived from aliphatic diacid dichlorides (so-called "soft-block" segments). In preferred embodiments n is zero and the arylate blocks comprise dicarboxylic acid residues derived from a mixture of iso- and terephthalic acid residues, wherein the molar ratio of isophthalate to terephthalate is about 0.25-4.0:1, preferably about 0.4-2.5:1, and more preferably about 0.67-1.5:1.

In the organic carbonate blocks, each R^5 is independently a divalent organic radical. Preferably, said radical comprises at least one dihydroxy-substituted aromatic hydrocarbon, and at least about 60 percent of the total number of R^5 groups in the polymer are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Suitable R^5 radicals include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)-phenylene, 2,2-bis(4-phenylene)propane, 6,6'-(3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indan]) and similar radicals such as those which correspond to the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent 4,217,438, which is incorporated herein by reference.

More preferably, each R⁵ is an aromatic organic radical and still more preferably a radical of Formula XI :



5 Formula XI

wherein each A¹ and A² is a monocyclic divalent aryl radical and Y is a bridging radical in which one or two carbon atoms separate A¹ and A². The free valence bonds in Formula XI are usually in the meta or para positions of A¹ and A² in relation to Y. Compounds in which R⁵ has Formula XI are bisphenols, and for the
10 sake of brevity the term "bisphenol" is sometimes used herein to designate the dihydroxy-substituted aromatic hydrocarbons. It should be understood, however, that non-bisphenol compounds of this type may also be employed as appropriate.

In Formula XI, A¹ and A² typically represent unsubstituted phenylene or
15 substituted derivatives thereof, illustrative substituents (one or more) being alkyl, alkenyl, and halogen (particularly bromine). Unsubstituted phenylene radicals are preferred. Both A¹ and A² are preferably p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

The bridging radical, Y, is one in which one or two atoms, separate A¹ from
20 A². The preferred embodiment is one in which one atom separates A¹ from A². Illustrative radicals of this type are -O-, -S-, -SO- or -SO₂-, methylene, cyclohexyl methylene, 2-[2.2.1]-bicycloheptyl methylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene, and like radicals.

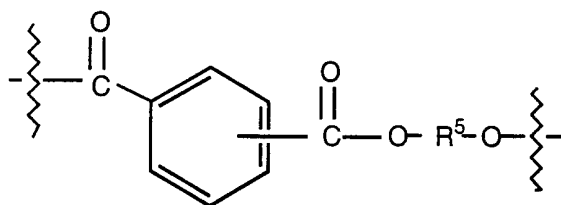
Gem-alkylene (commonly known as "alkylidene") radicals are preferred.
25 Also included, however, are unsaturated radicals. For reasons of availability and particular suitability for the purposes of this invention, the preferred bisphenol is 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A or BPA), in which Y is isopropylidene and A¹ and A² are each p-phenylene. Depending upon the molar excess of resorcinol
30 moiety present in the reaction mixture, R⁵ in the carbonate blocks may at least partially comprise resorcinol moiety. In other words, in some embodiments of the

invention carbonate blocks of Formula X may comprise a resorcinol moiety in combination with at least one other dihydroxy-substituted aromatic hydrocarbon.

Diblock, triblock, and multiblock copolyestercarbonates are encompassed in the present invention. The chemical linkages between blocks comprising resorcinol arylate chain members and blocks comprising organic carbonate chain members may
5 comprise at least one of

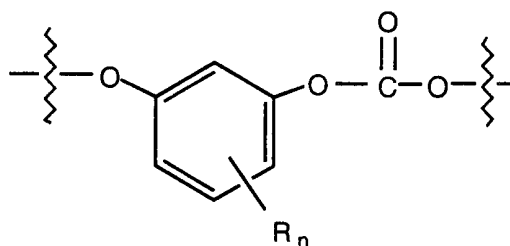
(a) an ester linkage between a suitable dicarboxylic acid residue of an arylate moiety and an $-O-R^5-O-$ moiety of an organic carbonate moiety, for example as typically illustrated in Formula XII, wherein R^5 is as previously defined :

10



Formula XII

and (b) a carbonate linkage between a diphenol residue of a resorcinol arylate moiety and a $-(C=O)-O-$ moiety of an organic carbonate moiety as shown in
15 Formula XIII, wherein R and n are as previously defined :



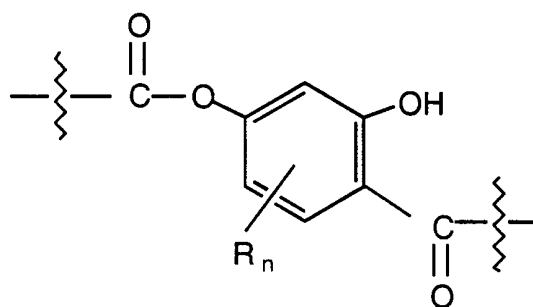
Formula XIII

The presence of a significant proportion of ester linkages of the type (a) may result in undesirable color formation in the copolyestercarbonates. Although the
20 invention is not limited by theory, it is believed that color may arise, for example, when R^5 in Formula XII is bisphenol A and the moiety of Formula XII undergoes Fries rearrangement during subsequent processing and/or light-exposure. In a preferred embodiment the copolyestercarbonate is substantially comprised of a

diblock copolymer with a carbonate linkage between resorcinol arylate block and an organic carbonate block. In a more preferred embodiment the copolyestercarbonate is substantially comprised of a triblock carbonate-ester-carbonate copolymer with carbonate linkages between the resorcinol arylate block and organic carbonate end-blocks.

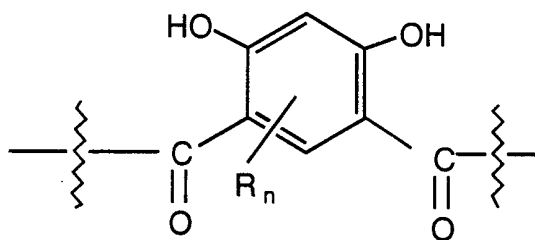
Copolyestercarbonates with at least one carbonate linkage between a thermally stable resorcinol arylate block and an organic carbonate block are typically prepared from resorcinol arylate-containing oligomers prepared by the method of the invention and containing at least one and preferably two hydroxy-terminal sites. Said oligomers typically have weight average molecular weight of about 10,000 to about 40,000, and more preferably about 15,000 to about 30,000. Thermally stable copolyestercarbonates may be prepared by reacting said resorcinol arylate-containing oligomers with phosgene, at least one chain-stopper, and at least one dihydroxy-substituted aromatic hydrocarbon in the presence of a catalyst such as a tertiary amine.

It is believed that the weatherability and certain other beneficial properties of the polymers comprising resorcinol arylate polyester chain members of the invention are attributable, at least in part, to the occurrence of thermally or photochemically induced Fries rearrangement of arylate blocks to yield o-hydroxybenzophenone moieties or analogs thereof which serve as stabilizers to UV radiation. More particularly, at least a portion of resorcinol arylate polyester chain members can rearrange to yield chain members with at least one hydroxy group ortho to at least one ketone group. Such rearranged chain members are typically o-hydroxybenzophenone-type chain members comprising one or more of the following structural moieties :

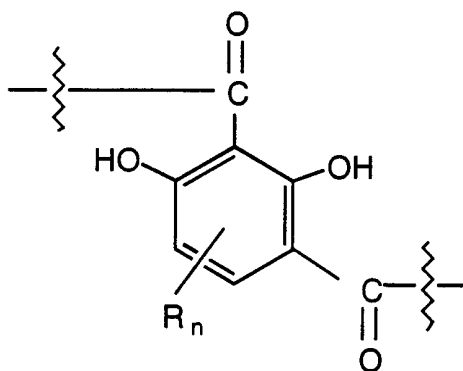


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Formula XIV



Formula XV



Formula XVI

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wherein R and n are as previously defined. The o-hydroxy-benzophenone-type chain members resulting from rearrangement of resorcinol arylate chain members can be present in resorcinol arylate polyesters and in resorcinol arylate polyester-containing copolymers, including resorcinol arylate-containing copolyestercarbonates and resorcinol arylate-containing copolyesters containing soft-blocks. It is also contemplated to introduce moieties of the types illustrated in Formulas XIV, XV, and XVI via synthesis and polymerization of appropriate monomers in both homopolymers and copolymers by the method of the present invention. In one embodiment the present invention provides thermally stable polyesters, copolyestercarbonates, and copolyesters comprising structural units represented by Formulas III and XIV, wherein the molar ratio of structural units represented by Formula III to structural units represented by Formula XIV ranges from about 99:1 to about 1:1, and preferably from about 99:1 to about 80:20.

15

The polymers and copolymers comprising thermally stable resorcinol arylate polyester chain members may also be employed as weatherability-improving additives in blends with at least one other polymer, especially polycarbonates

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(hereinafter sometimes designated "PC"), polyesters, polyetherimides, polyphenylene ethers, and addition polymers. Related blends are disclosed in commonly owned, co-pending application Serial No. 09/152,877, the disclosure of which is incorporated by reference herein.

5 The polycarbonates in the blend compositions of the invention are, for the most part, similar in molecular structure to the carbonate blocks of the block copolyestercarbonate as described hereinabove, with bisphenol-A homo- and copolycarbonates generally being preferred. Polyesters are illustrated by poly(alkylene dicarboxylates), especially poly(ethylene terephthalate) (hereinafter
10 sometimes designated "PET"), poly(1,4-butylene terephthalate) (hereinafter sometimes designated "PBT"), poly(trimethylene terephthalate) (hereinafter sometimes designated "PTT"), poly(ethylene naphthalate) (hereinafter sometimes designated "PEN"), poly(butylene naphthalate) (hereinafter sometimes designated "PBN"), poly(cyclohexanedimethanol terephthalate), poly(cyclohexanedimethanol-
15 co-ethylene terephthalate) (hereinafter sometimes designated "PETG"), and poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate) (hereinafter sometimes designated "PCCD"), and especially poly(alkylene arenedioates), with poly(ethylene terephthalate) and poly(1,4-butylene terephthalate) being preferred.

 Copolyestercarbonates may also be used in blends with polymers comprising
20 resorcinol arylate polyester chain members. Such copolymers comprise, in addition to the organic carbonate units, ester units such as isophthalate and/or terephthalate. The copolyester-carbonates which find use in the instant invention and the methods for their preparation are well known in the art as disclosed in, for example, U.S. Patent Nos. 3,030,331; 3,169,121; 3,207,814; 4,194,038; 4,156,069; 4,238,596; 4,238,597;
25 4,487,896; and 4,506,065.

 Suitable addition polymers include homopolymers and copolymers, especially homopolymers of alkenylaromatic compounds, such as polystyrene, including syndiotactic polystyrene, and copolymers of alkenylaromatic compounds with ethylenically unsaturated nitriles, such as acrylonitrile and methacrylonitrile; dienes,
30 such as butadiene and isoprene; and/or acrylic monomers, such as ethyl acrylate. These latter copolymers include the ABS (acrylonitrile-butadiene-styrene) and ASA (acrylonitrile-styrene-alkyl acrylate) copolymers.

 In another embodiment the invention encompasses blends of polymers and/or copolymers comprising thermally stable resorcinol arylate polyester chain members

with at least two other polymers. Said at least two other polymers may comprise miscible, immiscible, and compatibilized blends including, but not limited to, PC/ABS, PC/ASA, PC/PBT, PC/PET, PC/polyetherimide, polyester/polyetherimide, polyphenylene ether/polystyrene, polyphenylene ether/polyamide, and polyphenylene ether/polyester.

The blend compositions of the invention may be prepared by such conventional operations as solvent blending and melt blending. A particularly preferred method for blend preparation is melt blending such as by extrusion. The blends may additionally contain art-recognized additives including pigments, dyes, impact modifiers, UV screeners, flame retardants, fillers, stabilizers, flow aids, ester interchange inhibitors, and mold release agents. It is intended that the blend compositions include simple physical blends and any reaction products thereof, as illustrated, for example, by polyester-polycarbonate transesterification products.

Proportions of the polymers comprising resorcinol arylate polyester chain members in such blends are determined chiefly by the resulting proportions of arylate blocks, which most often comprise the active weatherability-improving entities, typical proportions providing about 10-50% by weight of arylate blocks in the blend. In blends where some degree of incompatibility may exist between the polymers comprising resorcinol arylate polyester chain members of the invention and the polycarbonates, polyesters, or addition polymers with which they may be combined, said blends are sometimes not fully transparent. However, transparent blends may often be prepared by adjusting the length of the arylate blocks in the polymers comprising resorcinol arylate polyester chain members. The other properties of said blends are generally excellent.

Compositions comprising resorcinol arylate polyester chain members made by the method of the invention typically have significantly lower color, both before and after thermal processing, than related compositions made by melt methods, interfacial methods, and solution methods of the prior art. In particular, melt methods typically provide resorcinol arylate polyester with tan to dark brown color while the present interfacial method provides very lightly colored or essentially colorless polyester. The present compositions may be used in various applications, especially those involving outdoor use and storage, and hence requiring resistance to weathering. Their light transmitting properties are often similar to those of polycarbonates. Thus, they are often substantially transparent and colorless, and may often be employed as

substitutes for polycarbonates in the fabrication of transparent sheet material when improved weatherability is mandated.

In another embodiment the present invention comprises multilayer articles comprising a substrate layer comprising at least one thermoplastic polymer, thermoset
5 polymer, cellulosic material, glass, ceramic, or metal, and at least one coating layer thereon, said coating layer comprising a thermally stable polymer comprising resorcinol arylate polyester chain members substantially free of anhydride linkages linking at least two mers of the polymer chain. Optionally, the multilayer articles may further comprise an interlayer, for example an adhesive interlayer, between any
10 substrate layer and any thermally stable polymer coating layer. Multilayer articles of the invention include, but are not limited to, those which comprise a substrate layer and a coating layer of said thermally stable polymer; those which comprise a substrate layer with a coating layer of said thermally stable polymer on each side of said substrate layer; and those which comprise a substrate layer and at least one
15 coating layer of said thermally stable polymer with at least one interlayer between a substrate layer and a coating layer. Any interlayer may be transparent and/or may contain an additive, for example a colorant or decorative material such as metal flake. If desired, an overlayer may be included over the coating layer of thermally stable polymer, for example to provide abrasion or scratch resistance. The substrate layer,
20 coating layer of thermally stable polymer, and any interlayers or overcoating layers are preferably in contiguous superposed contact with one another.

Within the context of the present invention it should be understood that any coating layer comprising a thermally stable polymer comprising resorcinol arylate polyester chain members will also include polymer comprising o-hydroxy-
25 benzophenone or analogous chain members resulting from Fries rearrangement of said resorcinol arylate chain members, for example after exposure of said coating layer to UV-light. Typically, a preponderance of polymer comprising o-hydroxybenzophenone or analogous chain members will be on that side or sides of said coating layer exposed to UV-light and will overlay in a contiguous superposed layer
30 or layers that polymer comprising unrearranged resorcinol arylate chain members. If it is worn away or otherwise removed, polymer comprising o-hydroxybenzophenone or analogous chain members is capable of regenerating or renewing itself from the resorcinol arylate-containing layer or layers, thus providing continuous protection for any UV-light sensitive layers.

The multilayer articles typically have outstanding initial gloss, improved initial color, weatherability, impact strength, and resistance to organic solvents encountered in their final applications. Said articles may also be recyclable by reason of the compatibility of the discrete layers therein.

5 The material of the substrate layer in the articles of this invention may be at least one thermoplastic polymer, whether addition or condensation prepared. Condensation polymers include, but are not limited to, polycarbonates, particularly aromatic polycarbonates, polyphenylene ethers, polyetherimides, polyesters (other than those employed for the coating layer, as defined hereinafter), and polyamides.
10 Polycarbonates and polyesters are frequently preferred.

Suitable polycarbonates include homopolycarbonates comprising structural units of the type described for the organic carbonate blocks in the copolyestercarbonates of the invention. The most preferred polycarbonates are bisphenol A homo- and copolycarbonates. Preferably, the weight average molecular
15 weight of the initial polycarbonate ranges from about 5,000 to about 100,000; more preferably, from about 25,000 to about 65,000.

The polycarbonate substrate may also be a copolyestercarbonate (other than that copolyestercarbonate employed for the coating layer as defined hereinafter). Such copolymers typically comprise, in addition to the organic carbonate units, ester
20 units such as isophthalate and/or terephthalate. The copolyestercarbonates which find use in the instant invention and the methods for their preparation are well known in the art as disclosed in, for example, U.S. Patent Nos. 3,030,331; 3,169,121; 3,207,814; 4,194,038; 4,156,069; 4,238,596; 4,238,597; 4,487,896; and 4,506,065.

Polyester substrates include, but are not limited to, poly(ethylene
25 terephthalate), poly(1,4-butylene terephthalate), poly(trimethylene terephthalate), poly(ethylene naphthalate), poly(butylene naphthalate), poly(cyclohexanedimethanol terephthalate), poly(cyclohexanedimethanol-co-ethylene terephthalate), and poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate).

Suitable addition polymer substrates include homo- and copolymeric aliphatic
30 olefin and functionalized olefin polymers such as polyethylene, polypropylene, poly(vinyl chloride), poly(vinyl chloride-co-vinylidene chloride), poly(vinyl fluoride), poly(vinylidene fluoride), poly(vinyl acetate), poly(vinyl alcohol), poly(vinyl butyral), poly(acrylonitrile), acrylic polymers such as those of

(meth)acrylamides or of alkyl (meth)acrylates such as poly(methyl methacrylate) ("PMMA"), and polymers of alkenylaromatic compounds such as polystyrenes, including syndiotactic polystyrene. The preferred addition polymers for many purposes are polystyrenes and especially the so-called ABS and ASA copolymers, which may contain thermoplastic, non-elastomeric styrene-acrylonitrile side chains grafted on an elastomeric base polymer of butadiene and alkyl acrylate, respectively.

Blends of any of the foregoing polymers may also be employed as substrates. Typical blends include, but are not limited to, those comprising PC/ABS, PC/ASA, PC/PBT, PC/PET, PC/polyetherimide, PC/polysulfone, polyester/polyetherimide, PMMA/acrylic rubber, polyphenylene ether-polystyrene, polyphenylene ether-polyamide or polyphenylene ether-polyester. Although the substrate layer may incorporate other thermoplastic polymers, the above-described polycarbonates and/or addition polymers still more preferably constitute the major proportion thereof.

The substrate layer in the multilayer articles of this invention may also comprise at least one of any thermoset polymer. Suitable thermoset polymer substrates include, but are not limited to, those derived from epoxys, cyanate esters, unsaturated polyesters, diallylphthalate, acrylics, alkyds, phenol-formaldehyde, novolacs, resoles, bismaleimides, PMR resins, melamine-formaldehyde, urea-formaldehyde, benzocyclobutanes, hydroxymethylfurans, and isocyanates. In one embodiment of the invention the thermoset polymer substrate further comprises at least one thermoplastic polymer, such as, but not limited to, polyphenylene ether, polyphenylene sulfide, polysulfone, polyetherimide, or polyester. Said thermoplastic polymer is typically combined with thermoset monomer mixture before curing of said thermoset.

In one embodiment of the invention a thermoplastic or thermoset substrate layer also incorporates at least one filler and/or pigment. Illustrative extending and reinforcing fillers, and pigments include silicates, zeolites, titanium dioxide, stone powder, glass fibers or spheres, carbon fibers, carbon black, graphite, calcium carbonate, talc, mica, lithopone, zinc oxide, zirconium silicate, iron oxides, diatomaceous earth, calcium carbonate, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crushed quartz, calcined clay, talc, kaolin, asbestos, cellulose, wood flour, cork, cotton and synthetic textile fibers, especially reinforcing fillers such as glass fibers and carbon fibers, as well as colorants such as metal flakes, glass flakes and beads, ceramic particles, other polymer particles, dyes and pigments which

may be organic, inorganic or organometallic. In another embodiment the invention encompasses multilayer articles comprising a filled thermoset substrate layer such as a sheet-molding compound (SMC).

The substrate layer may also comprise at least one cellulosic material
5 including, but not limited to, wood, paper, cardboard, fiber board, particle board, plywood, construction paper, Kraft paper, cellulose nitrate, cellulose acetate butyrate, and like cellulosic-containing materials. The invention also encompasses blends of at least one cellulosic material and either at least one thermoset polymer (particularly an adhesive thermoset polymer), or at least one thermoplastic polymer (particularly a
10 recycled thermoplastic polymer, such as PET or polycarbonate), or a mixture of at least one thermoset polymer and at least one thermoplastic polymer.

Multilayer articles encompassed by the invention also include those comprising at least one glass layer. Typically any glass layer is a substrate layer, although multilayer articles comprising a thermally stable polymer coating layer
15 interposed between a glass layer and a substrate layer are also contemplated. Depending upon the nature of coating and glass layers, at least one adhesive interlayer may be beneficially employed between any glass layer and any thermally stable polymer coating layer. The adhesive interlayer may be transparent, opaque or translucent. For many applications it is preferred that the interlayer be optically
20 transparent in nature and generally have a transmission of greater than about 60% and a haze value less than about 3% with no objectionable color.

Metal articles exposed to UV-light may exhibit tarnishing and other detrimental phenomena. Therefore, in another embodiment the invention encompasses multilayer articles comprising at least one metal layer as substrate layer.
25 Representative metal substrates include those comprising brass, copper, and other metals or metal-containing articles which may require protection from UV-light. Depending upon the nature of coating and metal layers, at least one adhesive interlayer may be beneficially employed between any metal layer and any thermally stable polymer coating layer.

30 Also present in the articles of the invention is at least one coating layer comprising a thermoplastic polymer comprising thermally stable resorcinol arylate polyester chain members prepared by the method of the present invention. More particularly, suitable coating layers comprise thermally stable resorcinol arylate polyesters, copolyesters, (particularly those containing soft-blocks),

copolyestercarbonates, and mixtures thereof. Copolyestercarbonates, when used in both substrate layer and in coating layer, are different from each other in molecular structure. More specifically, when the coating layer contains copolyestercarbonate with resorcinol arylate polyester blocks, then any ester blocks in the substrate
5 copolyestercarbonate layer will typically be derived from the same divalent organic radical as contained in the carbonate blocks.

It is also within the scope of the invention for other polymers to be present which are miscible in at least some proportions with the polymer coating layer comprising thermally stable resorcinol arylate polyester chain members. Illustrative
10 examples of at least partially miscible polymers include polyetherimide and polyesters such as PBT, PET, PTT, PEN, PBN, PETG, PCCD, and bisphenol A polyarylate. Preferably, the coating layer polymer consists essentially of thermally stable resorcinol arylate polyesters, copolyesters, or copolyestercarbonates.

Another aspect of the invention is a method for preparing a multilayer article
15 which comprises applying at least one thermally stable coating layer to a second layer, said second layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and said coating layer comprising a polymer comprising resorcinol arylate polyester chain members substantially free of anhydride linkages linking at least two mers of the polymer chain.

In the method of the invention, at least one thermally stable coating layer is
20 applied to a second layer, which may be the substrate layer or at least one intermediate layer ultimately to be disposed between the coating and substrate layers. An intermediate layer may generally comprise any of the materials suitable for use as the substrate or coating layer, and may further contain fillers and colorants such as
25 described hereinabove. When necessary, it may be specifically chosen so as to provide good adhesion between substrate and coating layers. Colorants of the previously described types may also be present in the coating layer.

Application of the at least one coating layer may be performed by solvent-casting. More preferably, application of said coating layer comprises fabrication of a
30 separate sheet thereof followed by application to the second layer, or by simultaneous production of both layers, typically in a melt process. Thus, there may be employed such methods as co-injection molding, coextrusion, overmolding, blow molding, multi-shot injection molding and placement of a film of the coating layer material on the surface of the second layer followed by adhesion of the two layers, typically in an

injection molding apparatus; e.g., in-mold decoration, or in a hot-press. These operations may be conducted under art-recognized conditions.

It is also within the scope of the invention to apply a structure comprising the coating layer and the second layer to a third, substrate layer, which is generally of a thermoplastic, thermoset, or cellulosic material similar or identical to that of the second layer but different from that of the coating layer. This may be achieved, for example, by charging an injection mold with the structure comprising the coating layer and the second layer and injecting the substrate sheet material behind it. By this method, in-mold decoration and the like are possible. Both sides of the substrate layer may receive the other layers, though it is usually preferred to apply them to only one side.

The thicknesses of the various layers in multilayer articles of this invention are most often as follows:

substrate—at least about 125 μ (microns), preferably at least about 250 μ , more preferably at least about 400 μ ,
coating—about 2-2,500, preferably about 10-250 and most preferably about 50-175 μ ,
second material, if any—about 2-2,500, preferably about 10-250, and most preferably about 50-175 μ ,
total—at least about 125 μ , preferably at least about 250 μ , more preferably at least about 400 μ .

The articles of this invention are characterized by the usual beneficial properties of the substrate layer, in addition to weatherability as evidenced by improved resistance to ultraviolet radiation and maintenance of gloss, and solvent resistance. Depending upon the coating layer/substrate combination, the multilayer articles may possess recycling capability, which makes it possible to employ the regrind material as a substrate for further production of articles of the invention.

Multilayer articles which can be made which comprise thermally stable polymers comprising resorcinol arylate polyester chain members include automotive, truck, military vehicle, and motorcycle exterior and interior components, including panels, quarter panels, rocker panels, trim, fenders, doors, decklids, trunklids, hoods, bonnets, roofs, bumpers, fascia, grilles, mirror housings, pillar appliques, cladding, body side moldings, wheel covers, hubcaps, door handles, spoilers, window frames,

headlamp bezels, headlamps, tail lamps, tail lamp housings, tail lamp bezels, license plate enclosures, roof racks, and running boards; enclosures, housings, panels, and parts for outdoor vehicles and devices; enclosures for electrical and telecommunication devices; outdoor furniture; aircraft components; boats and marine equipment, including trim, enclosures, and housings; outboard motor housings; depth finder housings, personal water-craft; jet-skis; pools; spas; hot-tubs; steps; step coverings; building and construction applications such as glazing, roofs, windows, floors, decorative window furnishings or treatments; treated glass covers for pictures, paintings, posters, and like display items; wall panels, and doors; protected graphics; outdoor and indoor signs; enclosures, housings, panels, and parts for automatic teller machines (ATM); enclosures, housings, panels, and parts for lawn and garden tractors, lawn mowers, and tools, including lawn and garden tools; window and door trim; sports equipment and toys; enclosures, housings, panels, and parts for snowmobiles; recreational vehicle panels and components; playground equipment; articles made from plastic-wood combinations; golf course markers; utility pit covers; computer housings; desk-top computer housings; portable computer housings; lap-top computer housings; palm-held computer housings; monitor housings; printer housings; keyboards; FAX machine housings; copier housings; telephone housings; mobile phone housings; radio sender housings; radio receiver housings; light fixtures; lighting appliances; network interface device housings; transformer housings; air conditioner housings; cladding or seating for public transportation; cladding or seating for trains, subways, or buses; meter housings; antenna housings; cladding for satellite dishes; coated helmets and personal protective equipment; coated synthetic or natural textiles; coated photographic film and photographic prints; coated painted articles; coated dyed articles; coated fluorescent articles; coated foam articles; and like applications. The invention further contemplates additional fabrication operations on said articles, such as, but not limited to, molding, in-mold decoration, baking in a paint oven, lamination, and/or thermoforming.

This invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

The invention is illustrated by the following, non-limiting examples. All parts are by weight unless otherwise designated. Molecular weight values for polymeric samples were determined by gel permeation chromatography (GPC) using 3% isopropanol/chloroform eluent at 0.75 milliliters (ml) per minute (min) on a Polymer

Labs Mixed C size exclusion column held at 35°C, and calibrated using polystyrene standards, and analyzed with Turbogel software.

EXAMPLE 1

This example illustrates the preparation of a thermally stable resorcinol arylate polyester with both iso- and terephthalate units. To a one liter, five neck, Morton flask blanketed with nitrogen and equipped with a mechanical stirrer, pH electrode, reflux condenser, two pressure equalizing addition funnels, was charged resorcinol (21.8 grams [g]; 0.198 moles [mol]), resorcinol monobenzoate capping agent (1.07 g; 2.5 mole %), triethylamine (0.274 ml; 1 mole %), dichloromethane (150 ml), and water (100 ml). One addition funnel was charged with sodium hydroxide pellets (16.84 g; 0.42 mol) and water (32 ml), while a solution of isophthaloyl dichloride (20.3 g; 0.1 mol), terephthaloyl dichloride (20.3 g; 0.1 mol), and dichloromethane (150 ml) was added to the second. The pH of the reaction mixture was adjusted to 7.5 with sodium hydroxide prior to the addition of acid chloride solutions, which were added over 6 minutes. The pH of the reaction was maintained between 7.25 and 7.75 for the first ten minutes of reaction. At 11 minutes the reaction the pH was raised to about 10 with the addition of sodium hydroxide and held for an additional 10 minutes. The stirring was stopped and the aqueous layer was removed. The resulting gray organic layer was washed with 1N hydrochloric acid, 0.1N hydrochloric acid, water (three times), and the polymer isolated by precipitation into boiling water yielding a white, fibrous material which was dried in vacuum at 110°C overnight. The isolated polymer was the desired resorcinol arylate polyester.

CONTROL EXAMPLE 1

A polyester of resorcinol with a mixture of iso- and terephthalate was prepared in a blender according to the interfacial method of U.S. Patent No. 3,460,961. The isolated polymer had weight average molecular weight of about 289,000. The procedure was modified by addition of 4 mole % chain-stopper (phenol), resulting in polymer with weight average molecular weight of about 51,000.

CONTROL EXAMPLE 2

A polyester of resorcinol with a mixture of iso- and terephthalate was prepared according to the solution method of Cohen et al., Journal of Polymer Science : Part A-1, vol. 9, 3263-3299 (1971). To a one-liter, three neck, round bottomed flask equipped with a mechanical stirrer and an addition funnel were

charged isophthaloyl chloride (5.076 g, 25 millimoles [mmol]), terephthaloyl chloride (5.076 g, 25 mmol), resorcinol (5.506 g, 50 mmol), and tetrahydrofuran (200 ml) dried by distillation from sodium and benzophenone. Polymerization was initiated by dropwise addition of a stoichiometric amount of triethylamine (10.12 g, 10 mmol) over 30 minutes. The mixture then was stirred for 3 hours at room temperature. Triethylamine hydrochloride was removed from the reaction mixture by filtration. The filtrate was slowly poured into methanol (500 ml) in a blender. The precipitated polymer was washed with hot water and dried in a vacuum oven. The isolated polymer had weight average molecular weight of about 47,000.

10 EXAMPLES 2-11

These examples illustrate the preparation of hydroxy-terminated resorcinol iso/terephthalate oligomers. Into a 1 liter Morton flask equipped with a mechanical stirrer, pH electrode, condenser, and two addition tubes connected to metering pumps were charged resorcinol (12.11 g, 0.11 mol), water (18 ml), methylene chloride (200 ml), and triethylamine (140 to 560 microliters, 1 to 4 mol % based on acid chlorides). The mixture was stirred at 500 rpm. A two-step addition profile was used for the delivery of acid chloride solution and base solution. In the first step, a majority of base (60 to 80 % out of total base amount of 17.5 ml of 33% aqueous sodium hydroxide solution) and the whole acid chloride solution (70 ml solution of isophthaloyl chloride (10.15 g, 0.05 mol) and terephthaloyl chloride (10.15 g, 0.05 mol) in methylene chloride) were added at constant rates, and the remaining base was added in the second step at continuously decreasing rate. The base was pumped from graduated burets and the amount was checked every 30 seconds in order to control the stoichiometry. The pH varied between about 3.5 and about 8. The length of the first step was varied from 7 to 13 minutes with the total step 1 and step 2 time constant at 25 minutes. The reaction mixture was further stirred for 30 minute total reaction time. The reaction conditions and weight average molecular weights of the isolated polymers are shown in Table 1.

30

TABLE 1

| Example | % Base Added in 1st Step | Base Addition time (min.) | mol % triethylamine | Oligomer Mw ^a |
|---------|--------------------------|---------------------------|---------------------|--------------------------|
| 2 | 60 | 7 | 1 | 27.3 |
| 3 | 60 | 7 | 4 | 26.9 |
| 4 | 60 | 13 | 4 | 24.5 |
| 5 | 60 | 13 | 1 | 26 |
| 6 | 70 | 10 | 2.5 | 28.3 |
| 7 | 70 | 10 | 2.5 | 23 |
| 8 | 80 | 7 | 4 | 28.4 |
| 9 | 80 | 7 | 1 | 30.8 |
| 10 | 80 | 13 | 4 | 29.5 |
| 11 | 80 | 13 | 1 | 30.4 |

^a times 10⁻³

5 A sample of each polymer was analyzed for anhydride content by treatment in solution with diisobutylamine. Polymers prepared using 4 mol % triethylamine showed greater than 95% retention of weight average molecular weight.

EXAMPLES 12-28

10 The procedure of Examples 2-11 was repeated except that in some experiments 13 to 15 mol % total excess of resorcinol was used. In some experiments a small amount of capping agent (1 mol % phenol) was added. In some cases, the reaction mixture was heated externally to a refluxing point at 3 minutes. The reaction conditions and weight average molecular weights of the isolated polymers are shown in Table 2.

15

20

25

TABLE 2

| Example | mol % triethylamine | Comments ^a | Reflux ^b | Initial Mw ^c | % Mw Retention ^d |
|---------|------------------------|-----------------------|---------------------|----------------------------|--------------------------------|
| 12 | 4 | 1% PhOH | Y | 19.5 | 99 |
| 13 | 4 | 15% excess Rs | N | 19.9 | 100 |
| 14 | 4 | 0.5% PhOH | N | 21.6 | 99.5 |
| 15 | 4 | 15% excess Rs | Y | 21.8 | 96.6 |
| 16 | 4 | 1% PhOH | N | 21.9 | 99.3 |
| 17 | 4 | 1% PhOH | Y | 22.2 | 97.7 |
| 18 | 4 | | N | 22.3 | 96.1 |
| 19 | 4 | 13% excess Rs | N | 22.4 | 97.7 |
| 20 | 4 | 1% PhOH | Y | 22.4 | 96.4 |
| 21 | 4 | 1% PhOH | Y | 22.5 | 93 |
| 22 | 4 | 1% PhOH | N | 22.7 | 97.8 |
| 23 | 4 | 0.5 PhCOCl | N | 24.6 | 99 |
| 24 | 2.5 | 1% PhOH | Y | 24.7 | 97.2 |
| 25 | 4 | | N | 24.8 | 96.7 |
| 26 | 4 | | Y | 25.3 | 98 |
| 27 | 4 | | N | 26.6 | 97.7 |
| 28 | 3 | | Y | 30.3 | 100 |

- 5 ^a PhOH (phenol); Rs (resorcinol); PhCOCl (benzoyl chloride)
^b Y (Yes); N (No)
^c times 10⁻³
^d following treatment with diisobutylamine in solution

EXAMPLES 29-46

- 10 The procedure of Examples 2-11 was repeated except that a portion of
tertiary amine was added following addition of dicarboxylic acid dichloride to
resorcinol moiety. A total of 4 mol % tertiary amine (40000 ppm; based on moles
acid chlorides) was added. The reaction conditions and weight average molecular
weights of the isolated polymers are shown in Table 3. Example 46 is a control
15 experiment in which all the tertiary amine was present at the beginning of the reaction
before addition of dicarboxylic acid dichloride to resorcinol moiety

TABLE 3

| Example | % Base Added in 1st Step | Base Addition time (min.) | TEA added initially (ppm) | Initial Mw ^a | % Mw Retention ^b |
|---------|--------------------------|---------------------------|---------------------------|-------------------------|-----------------------------|
| 29 | 80 | 7 | 50 | 29.3 | 96.5 |
| 30 | 80 | 7 | 10 | 23.1 | 86.8 |
| 31 | 80 | 7 | 10 | 22.2 | 98.5 |
| 32 | 80 | 7 | 50 | 29.4 | 97.4 |
| 33 | 96 | 7 | 10 | 32.7 | 94.3 |
| 34 | 96 | 7 | 50 | 34.4 | 92.5 |
| 35 | 88 | 10 | 30 | 26.5 | 99.4 |
| 36 | 88 | 10 | 30 | 25.6 | 101 |
| 37 | 80 | 13 | 50 | 25.9 | 95.9 |
| 38 | 80 | 13 | 10 | 25.2 | 96.6 |
| 39 | 96 | 13 | 50 | 29.4 | 90.2 |
| 40 | 96 | 13 | 10 | 22.14 | 98.59 |
| 41 | 96 | 13 | 50 | 26.7 | 92.93 |
| 42 | 96 | 13 | 10 | 23.6 | 90.5 |
| 43 | 96 | 16 | 10 | 21.6, 22.0 | 98.8, 98.0 |
| 44 | 96 | 19 | 10 | 24.1, 22.3 | 95.9, 97.3 |
| 45 | 64 | 7 | 10 | 21.46, 23.31 | 96.3, 100 |
| 46 | 96 | 16 | 40000 | 24.7, 23.1 | 92.7, 94.4 |

^a times 10⁻³

5 ^b following treatment with diisobutylamine in solution

EXAMPLE 47

This example illustrates the preparation of a thermally stable resorcinol iso/terephthalate-block-copolycarbonate beginning with the preparation of hydroxy-terminated resorcinol iso/terephthalate oligomer. To a thirty liter glass reactor equipped with a glass impeller, centrifuge recirculation pump, reflux condenser and pressure-equilibration addition funnel were charged resorcinol (605.6 g, 5.5 mol), methyltributylammonium chloride (82.5 g of a 75% wt. aqueous solution; 0.275 mol), dichloromethane (6.5 liters), and water (2.5 liters). The recirculation pump was turned on and the mixture was degassed with nitrogen while stirring. The pH of the aqueous phase was adjusted to 7 with 50% aqueous sodium hydroxide solution. Reaction was carried out by adding a solution of acid chlorides (507.5 g each of iso- and terephthaloyl dichlorides; 5.00 moles total in 2.0 liters of dichloromethane solution) while stirring and simultaneously adding 50% sodium hydroxide solution at such a rate that the pH was maintained between 6 and 8. The acid chlorides were added

using a three-step program with the rate of addition declining with each step. A timer was started at the beginning of acid chloride addition. The pH was maintained at 8 while adding acid chlorides over 8 minutes using the following protocol: 40% of total acid chlorides was added over the first 2 minutes; 30% of total was added over
5 the next 2 minutes; the remaining 30% of total was added over the next 4 minutes. The recirculation loop was running during the entire time.

Following complete addition of acid chlorides, the pH was slowly raised to 11-12 over two to three minutes, and the reaction mixture was stirred for 10 minutes. The polymer formed was a hydroxy-terminated oligomer with weight average
10 molecular weight (Mw) of approximately 20,000.

Bisphenol A (1102 g, 4.83 mol), dichloromethane (4.0 liters), triethylamine (17 ml, 0.12 mol), p-cumyl phenol capping agent (60 g), and water (6.0 liters) were then added and the recirculation loop was turned on. Phosgene was introduced at pH 7.5-8.5, then increasing slowly to pH 10-10.5 using a 15% excess over the theoretical
15 amount of phosgene.

The reaction mixture was separated, the organic phase washed with 1N hydrochloric acid, 0.1N hydrochloric acid, and twice with water, and the polymer was isolated by precipitation in methanol. The polymer obtained was the desired resorcinol iso/terephthalate-co-BPA polycarbonate copolymer.

20 EXAMPLES 48-61

Samples of polymers comprising resorcinol arylate polyester chain members were dried in vacuo at 120°C for 15 hrs. A weighed sample of about 25-30 milligrams was placed in a circular die cavity 2 centimeters (cm.) in diameter and covered with a cylindrical piston of the same size. The die assembly containing the
25 sample was heated in a Carver press at 290°C for 5 minutes at 500-4,000 pounds gauge (lbs.g.) pressure, then removed and cooled in chill blocks. The heat treatment produced a film about 1 mil in thickness and 2 cm. in diameter. Molecular weights of samples before and after the heat treatment were measured by GPC using polystyrene standards. Table 4 shows examples of melt stability for resorcinol arylate polyesters
30 prepared using the method of Example 1 and Control Examples 1 and 2, and for resorcinol arylate-containing copolyestercarbonates prepared using the method of Example 47. Wt.% resorcinol arylate in the Table refers to wt.% resorcinol arylate chain members in the polymer, the remaining mers being organic carbonate mers.

TABLE 4

| Example | wt.% resorcinol arylate | % Mw Retention, melt processing ^f | % Mw Retention, amine test ^g |
|-----------------|-------------------------------|---|---|
| 48 ^a | 50 | 89.4 | 98 |
| 49 ^a | 80 | 84 | 97.9 |
| 50 ^a | 50 | 84.8 | 94 |
| 51 ^b | 50 | 98.8 | 99.5 |
| 52 ^b | 35 | 98.7 | 99.3 |
| 53 ^a | 100 | 55 | 62 |
| 54 ^a | 100 | 55.9 | 61 |
| 55 ^a | 100 | 45 | 40 |
| 56 ^b | 100 | 87.5 | 86 |
| 57 ^b | 100 | 97.7 | 99.6 |
| 58 ^b | 100 | 99.5 | 99 |
| 59 ^c | 100 | 12 | 25 |
| 60 ^d | 100 | 46 | 74 |
| 61 ^e | 100 | 77 | 78 |

- 5 ^a final reaction mixture stirred 5 min at pH 10
^b final reaction mixture stirred 20 min at pH 10-12
^c Control Example 1
^d Control Example 1 using 4 mole % phenol chain-stopper
10 ^e Control Example 2
^f following extrusion
^g following treatment with diisobutylamine in solution

EXAMPLE 62

A resorcinol arylate polyester was prepared by the interfacial method of Control Example 1 except that the organic solvent was dichloromethane and a capping agent was present. Extrusion of the material gave orange pellets. The polymer had initial weight average molecular weight (Mw) of 61,300 and Mw after extrusion of 52,200 (85% retention). A separate sample of material was treated with dibutylamine in solution; the Mw of the recovered material was 42,400 (69% retention).

20

EXAMPLE 63

A resorcinol arylate polyester was prepared by the method of Example 1. Extrusion of the material gave yellowish pellets. The polymer had initial Mw of 53,600 and Mw after extrusion of 50,800 (95% retention). A separate sample of material was treated with dibutylamine in solution; the Mw of the recovered material was 48,400 (90% retention).

EXAMPLE 64

A resorcinol arylate-containing block copolyester-carbonate with 50% by weight carbonate blocks and 1:1 ratio of isophthalate to terephthalate in the resorcinol arylate blocks was prepared by the method of Example 47 except that the resorcinol arylate-containing polyester block was made using the procedure of Control Example 1 using a capping agent and dichloromethane as the organic solvent. Extrusion of the material gave amber pellets. The copolymer had initial Mw of 75,900 and Mw after extrusion of 64,500 (85% retention). A separate sample of material was treated with dibutylamine in solution; the Mw of the recovered material was 73,000 (96% retention).

EXAMPLE 65

A resorcinol arylate-containing block copolyester-carbonate was prepared by the method of Example 47 with 50% by weight carbonate blocks and 1:1 ratio of isophthalate to terephthalate in the resorcinol arylate blocks. Extrusion of the material gave faintly yellowish pellets. The copolymer had initial Mw of 52,300 and Mw after extrusion of 51,700 (99% retention). A separate sample of material was treated with dibutylamine in solution; the Mw of the recovered material was 51,500 (98% retention).

Disks were formed from the resorcinol arylate-containing polymers of Examples 62-65. The disks were approximately 0.6 millimeters (mm) (0.024 inches) thick and 50 mm (2.0 inches) diameter, and were formed from melt-processed polymer (either pellets, extruded film, or injection molded parts) under the following conditions: 2.1 g of melt-processed polymer were placed in a mold between heated platens of a hydraulic press and heated at about 200°C with no applied pressure for 3 minutes, then under 4500 lbs.g. pressure for 1 minute, and finally under 6500 lbs.g.

pressure for 1 minute. The mold was then rapidly cooled in ice water and opened to remove the disk.

The disks prepared as described were laminated onto injection-molded plaques of LEXAN 140 polycarbonate (from General Electric Plastics) containing 2 wt.% of TiO₂ pigment under the following conditions to make well-adhered multilayer articles. All materials were placed in a heated (60°C) vacuum desiccator overnight. A disk was placed onto an injection molded plaque of polycarbonate 2.5 inches square and one-eighth inch thick in a mold between heated platens of a hydraulic press and heated at about 200°C with no applied pressure for 2 minutes, then under 4500 lbs.g. pressure for 1 minute, and finally under 6500 lbs.g. pressure for 1 minute. All samples were well adhered.

The color of the disks and of the laminated plaques was determined on a Macbeth 7000 Color-Eye colorimeter and reported as CIELAB values and yellowness index (YI; according to ASTM D1925). Results are shown on Table 5.

TABLE 5

| Example | Disks (transmission) | | | | Laminate on PC (reflection) | | | |
|----------------|----------------------|-------|------|-------|-----------------------------|-------|-------|-------|
| | L* | a* | b* | YI | L* | a* | b* | YI |
| 62 | 90.45 | -1.23 | 15.2 | 26.01 | 76.6 | 3.57 | 31.74 | 61.07 |
| 63 | 94.73 | -0.3 | 3.61 | 6.34 | 86.18 | -0.38 | 14.95 | 27.4 |
| 64 | 93.82 | -0.43 | 5.4 | 9.5 | 84.21 | 0.88 | 20.44 | 38.27 |
| 65 | 95.52 | -0.11 | 1.31 | 2.26 | 91.21 | -0.8 | 6.95 | 12 |
| unlaminated PC | | | | | 94.86 | -0.52 | 2.88 | 4.51 |

The data show that the disks and multilayer articles formed from melt-processed resorcinol arylate-containing polymers made by the method of the invention have much less color and lower yellowness index than the respective control blends.

WHAT IS CLAIMED IS:

1. An interfacial method for preparing polymers comprising resorcinol arylate polyester chain members substantially free of anhydride linkages linking at least two mers of the polymer chain, comprising the steps of :
 - 5 (a) combining at least one resorcinol moiety and at least one catalyst in a mixture of water and at least one organic solvent substantially immiscible with water; and
 - (b) adding to the mixture from (a) at least one dicarboxylic acid dichloride while maintaining the pH between 3 and 8.5 through the presence of an acid acceptor,
10 wherein the total molar amount of acid chloride groups is stoichiometrically deficient relative to the total molar amount of phenolic groups.
2. The method of claim 1 further comprising the step of : adjusting the pH of the reaction mixture to between 7 and 12 following addition of the at least one dicarboxylic acid dichloride.
- 15 3. The method of claim 2 further comprising the step of : stirring the reaction mixture for at least 3 minutes at pH between 7 and 12.
4. The method of claim 1 wherein the at least one resorcinol moiety is selected from the group consisting of unsubstituted resorcinol, 2-methyl resorcinol, and mixtures thereof.
- 20 5. The method of claim 4 wherein the at least one resorcinol moiety is unsubstituted resorcinol.
6. The method of claim 1 wherein the at least one catalyst is selected from the group consisting of tertiary amines, quaternary ammonium salts, quaternary phosphonium salts, hexaalkylguanidinium salts, and mixtures thereof.
- 25 7. The method of claim 6 wherein the at least one catalyst is selected from the group consisting of triethylamine, dimethylbutylamine, N-ethylpiperidine, N-methylpiperidine, diisopropylethyl amine, 2,2,6,6-tetramethylpiperidine, tetrapropylammonium bromide, tetrabutylammonium bromide, tetrabutylammonium chloride, methyltributylammonium chloride, benzyltriethylammonium chloride,

cetyltrimethylammonium bromide, tetrabutylphosphonium bromide, hexaethylguanidinium chloride, and mixtures thereof.

8. The method of claim 6 wherein the catalyst is at least one tertiary amine.
- 5 9. The method of claim 8 wherein all tertiary amine is present before addition of dicarboxylic acid dichloride to resorcinol moiety.
10. The method of claim 8 wherein a portion of any tertiary amine is added following addition of dicarboxylic acid dichloride to resorcinol moiety.
- 10 11. The method of claim 1 wherein the at least one organic solvent is selected from the group consisting of chloroform, chlorobenzene, dichloromethane, 1,2-dichloroethane, dichlorobenzene, toluene, xylene, trimethylbenzene, and mixtures thereof.
- 15 12. The method of claim 1 wherein the at least one dicarboxylic acid dichloride is selected from the group consisting of isophthaloyl dichloride, terephthaloyl dichloride, naphthalene-2,6-dicarboxylic acid dichloride, and mixtures thereof.
13. The method of claim 12 further comprising at least one aliphatic dicarboxylic acid dichloride.
- 20 14. The method of claim 13 wherein the at least one aliphatic dicarboxylic acid dichloride is selected from the group consisting of sebacoyl chloride and cyclohexane-1,4-dicarboxylic acid dichloride.
15. The method of claim 12 wherein the at least one dicarboxylic acid dichloride is a mixture of isophthaloyl dichloride and terephthaloyl dichloride.
- 25 16. The method of claim 15 wherein the ratio of isophthaloyl dichloride to terephthaloyl dichloride is about 0.2-5 : 1.
17. The method of claim 16 wherein the ratio of isophthaloyl dichloride to terephthaloyl dichloride is about 0.8-2.5 : 1.
18. The method of claim 1 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.5-1.01 : 1.

19. The method of claim 18 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.2-1.02 : 1.
20. The method of claim 1 wherein the pH is maintained using an alkali metal hydroxide, an alkaline earth hydroxide, or an alkaline earth oxide.
- 5 21. The method of claim 20 wherein the pH is maintained using aqueous sodium hydroxide.
22. The method of claim 1 wherein the pH is maintained through simultaneous addition of acid acceptor with the at least one dicarboxylic acid dichloride.
- 10 23. The method of claim 1 further comprising at least one chain-stopper selected from the group consisting of mono-phenolic compounds, mono-carboxylic acid chlorides, mono-chloroformates, and mixtures thereof.
24. The method of claim 23 wherein the at least one chain-stopper is at least one mono-phenolic compound selected from the group consisting of phenol,
15 alkyl-substituted phenol, p-cumylphenol, p-tertiary-butyl phenol, diphenol monoester, resorcinol monobenzoate, diphenol monoether, and p-methoxyphenol.
25. The method of claim 24 wherein the at least one mono-phenolic compound is present with the at least one resorcinol moiety.
26. The method of claim 23 wherein the at least one chain-stopper is at
20 least one mono-carboxylic acid chloride selected from the group consisting of benzoyl chloride, alkyl-substituted benzoyl chloride, toluoyl chloride, halogen-substituted benzoyl chloride, bromobenzoyl chloride, trimellitic anhydride chloride, cinnamoyl chloride, 4-nadimidobenzoyl chloride, and mixtures thereof.
27. The method of claim 26 wherein the at least one mono-carboxylic acid
25 chloride is present with the at least one dicarboxylic acid dichloride.
28. The method of claim 23 wherein the at least one chain-stopper is at least one mono-chloroformate selected from the group consisting of phenyl chloroformate, alkyl-substituted phenyl chloroformate, p-cumyl phenyl chloroformate, toluene chloroformate, and mixtures thereof.

29. The method of claim 28 wherein the at least one mono-chloroformate is present with the at least one dicarboxylic acid dichloride.
30. The method of claim 1 wherein the polymer is recovered from the mixture.
- 5 31. The polymer made by the method of claim 1.
32. The polymer made by the method of claim 5.
33. The polymer made by the method of claim 15.
34. The polymer made by the method of claim 23.
35. A multilayer article comprising:
- 10 a substrate layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and
- at least one coating layer thereon, said coating layer comprising the polymer made by the method of claim 1.
36. The article according to claim 35 wherein the substrate comprises at
- 15 least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.
37. The article according to claim 36 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.
- 20 38. The article according to claim 35 wherein the coating layer further comprises at least one colorant.
39. The article according to claim 35 wherein the substrate contains at least one of fillers and colorants.
40. The article according to claim 35 further comprising an intermediate
- 25 layer disposed between said coating and substrate layers.
41. The article according to claim 40 wherein the intermediate layer contains at least one of fillers and colorants.

42. The article according to claim 35 which is an automotive, truck, military vehicle, or motorcycle exterior or interior component, panel, quarter panel, rocker panel, trim, fender, door, decklid, trunklid, hood, bonnet, roof, bumper, fascia, grill, mirror housing, pillar applique, cladding, body side molding, wheel cover, hubcap, door handle, spoiler, window frame, headlamp bezel, headlamp, tail lamp, tail lamp housing, tail lamp bezel, license plate enclosure, roof rack, or running board; an enclosure, housing, panel, part, or trim for an outdoor vehicle or device, an electrical or telecommunication device, network interface device, outdoor furniture, aircraft, boat or marine equipment, outboard motor, depth finder, personal water-craft, jet-ski, pool, spa, hot-tub, step, or step covering, an automatic teller machine (ATM), a lawn or garden tractor, lawn mower, tool, sporting equipment or toy, snowmobile, recreational vehicle, golf course marker, or playground equipment; an enclosure, housing, panel, part, or trim for a computer, desk-top computer, portable computer, lap-top computer, palm-held computer, monitor, printer, keyboard, FAX machine, copier, telephone, mobile phone, radio sender, radio receiver, meter, antenna, light fixture, lighting appliance, transformer, air conditioner; an article used in building or construction, glazing, roofing, window, window trim, floor, wall panel, door, door trim, decorative window furnishing or treatment; a treated glass cover for a picture, painting, poster, or display item; a protected graphic; an outdoor or indoor sign; an article made from a plastic-wood combination; a utility pit cover; cladding or seating for public transportation; cladding or seating for trains, subways, or buses; cladding for satellite dishes; coated helmet or personal protective equipment; coated synthetic or natural textiles; coated photographic film or photographic print; coated painted article; coated dyed article; coated fluorescent article; or coated foam article.

43. A method for preparing a multilayer article which comprises applying at least one thermally stable coating layer to a second layer, said second layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and said coating layer comprising the polymer made by the method of claim 1.

44. The method according to claim 43 wherein the substrate comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

45. The method according to claim 44 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

46. The method according to claim 43 wherein the coating layer further
5 comprises at least one colorant.

47. The method according to claim 43 wherein the substrate contains at least one of fillers and colorants.

48. The method according to claim 43 further comprising an intermediate layer disposed between said coating and substrate layers.

10 49. The method according to claim 48 wherein the intermediate layer contains at least one of fillers and colorants.

50. The method according to claim 43 wherein said multilayer article is further applied to a substrate layer.

15 51. The method according to claim 50 wherein the substrate layer comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

52. A polymer consisting essentially of resorcinol arylate polyester chain members substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method, comprising the steps of :

20 (a) combining at least one resorcinol moiety and at least one catalyst in a mixture of water and at least one organic solvent substantially immiscible with water; and

(b) adding to the mixture from (a) at least one dicarboxylic acid dichloride while maintaining the pH between 3 and 8.5 through the presence of an acid acceptor,
25 wherein the total molar amount of acid chloride groups is stoichiometrically deficient relative to the total molar amount of phenolic groups.

53. The polymer of claim 52, prepared by an interfacial method further comprising the step of : adjusting the pH of the reaction mixture to between 7 and 12 following addition of the at least one dicarboxylic acid dichloride.

54. The polymer of claim 53, prepared by an interfacial method further comprising the step of : stirring the reaction mixture for at least 3 minutes at pH between 7 and 12.

55. The polymer of claim 52 wherein the at least one resorcinol moiety is selected from the group consisting of unsubstituted resorcinol, 2-methyl resorcinol, and mixtures thereof.

56. The polymer of claim 55 wherein the at least one resorcinol moiety is unsubstituted resorcinol.

57. The polymer of claim 52 wherein the at least one dicarboxylic acid dichloride is selected from the group consisting of isophthaloyl dichloride, terephthaloyl dichloride, naphthalene-2,6-dicarboxylic acid dichloride, and mixtures thereof.

58. The polymer of claim 57 wherein the at least one dicarboxylic acid dichloride is a mixture of isophthaloyl dichloride and terephthaloyl dichloride.

59. The polymer of claim 58 wherein the ratio of isophthaloyl dichloride to terephthaloyl dichloride is about 0.2-5 : 1.

60. The polymer of claim 59 wherein the ratio of isophthaloyl dichloride to terephthaloyl dichloride is about 0.8-2.5 : 1.

61. The polymer of claim 52 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.5-1.01 : 1.

62. The polymer of claim 61 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.2-1.02 : 1.

63. The polymer of claim 52 prepared by an interfacial method wherein the pH is maintained using an alkali metal hydroxide, an alkaline earth hydroxide, or an alkaline earth oxide.

64. The polymer of claim 63 prepared by an interfacial method wherein the pH is maintained using aqueous sodium hydroxide.

65. The polymer of claim 52 further comprising at least one chain-stopper selected from the group consisting of mono-phenolic compounds, mono-carboxylic acid chlorides, mono-chloroformates, and mixtures thereof.
66. The polymer of claim 52 wherein the molecular weight of said polymer decreases by less than 30% upon heating said polymer at a temperature of about 280-290°C for five minutes.
67. The polymer of claim 66 wherein the molecular weight of said polymer decreases by less than 10% upon heating at a temperature of about 280-290°C for five minutes.
68. A polymer consisting essentially of resorcinol arylate polyester chain members substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method, comprising the steps of :
- (a) combining at least one of unsubstituted resorcinol and 2-methylresorcinol; at least one catalyst selected from the group consisting of quaternary ammonium salts and tertiary amines; and at least one mono-phenolic chain-stopper in a mixture of water and dichloromethane;
 - (b) adding to the mixture from (a) a mixture of isophthaloyl dichloride and terephthaloyl dichloride in a molar ratio of isophthalate to terephthalate of 0.4-2.5 : 1, while maintaining the pH between 3 and 8.5 through addition of aqueous sodium hydroxide, wherein the ratio of moles total acid chloride groups to moles total phenolic groups is 1.5-1.01 : 1;
 - (c) adjusting the pH of the reaction mixture to between 8.5 and 10 following addition of the dicarboxylic acid dichloride mixture, and stirring the reaction mixture for at least 3 minutes at said pH; and
 - (d) isolating the polymer, said polymer decreasing in molecular weight by less than 30% upon heating at a temperature of about 280-290°C for five minutes.
69. A multilayer article comprising:
- a substrate layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and

at least one coating layer thereon, said coating layer comprising the polymer according to claim 66.

5 70. The article according to claim 69 wherein the substrate comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound

71. The article according to claim 70 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

10 72. The article according to claim 69 wherein the coating layer further comprises at least one colorant.

73. The article according to claim 69 wherein the substrate contains at least one of fillers and colorants.

74. The article according to claim 69 further comprising an intermediate layer disposed between said coating and substrate layers.

15 75. The article according to claim 74 wherein the intermediate layer contains at least one of fillers and colorants.

20 76. The article according to claim 69 which is an automotive, truck, military vehicle, or motorcycle exterior or interior component, panel, quarter panel, rocker panel, trim, fender, door, decklid, trunklid, hood, bonnet, roof, bumper, fascia, grill, mirror housing, pillar applique, cladding, body side molding, wheel cover, hubcap, door handle, spoiler, window frame, headlamp bezel, headlamp, tail lamp, tail lamp housing, tail lamp bezel, license plate enclosure, roof rack, or running board; an enclosure, housing, panel, part, or trim for an outdoor vehicle or device, an electrical or telecommunication device, network interface device, outdoor furniture, aircraft, boat or marine equipment, outboard motor, depth finder, personal water-craft, jet-ski, pool, spa, hot-tub, step, or step covering, an automatic teller machine (ATM), a lawn or garden tractor, lawn mower, tool, sporting equipment or toy, snowmobile, recreational vehicle, golf course marker, or playground equipment; an enclosure, housing, panel, part, or trim for a computer, desk-top computer, portable computer, lap-top computer, palm-held computer, monitor, printer, keyboard, FAX machine, copier, telephone, mobile phone, radio sender, radio receiver, meter, antenna, light fixture, lighting appliance, transformer, air conditioner; an article used

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in building or construction, glazing, roofing, window, window trim, floor, wall panel, door, door trim, decorative window furnishing or treatment; a treated glass cover for a picture, painting, poster, or display item; a protected graphic; an outdoor or indoor sign; an article made from a plastic-wood combination; a utility pit cover; cladding or seating for public transportation; cladding or seating for trains, subways, or buses; cladding for satellite dishes; coated helmet or personal protective equipment; coated synthetic or natural textiles; coated photographic film or photographic print; coated painted article; coated dyed article; coated fluorescent article; or coated foam article.

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77. A method for preparing a multilayer article which comprises applying at least one thermally stable coating layer to a second layer, said second layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and said coating layer comprising the polymer according to claim 66.

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78. The method according to claim 77 wherein the substrate comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

79. The method according to claim 78 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

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80. The method according to claim 77 wherein the coating layer further comprises at least one colorant.

81. The method according to claim 77 wherein the substrate contains at least one of fillers and colorants.

25
82. The method according to claim 77 further comprising an intermediate layer disposed between said coating and substrate layers.

83. The method according to claim 82 wherein the intermediate layer contains at least one of fillers and colorants.

84. The method according to claim 77 wherein said multilayer article is further applied to a substrate layer.

85. The method according to claim 84 wherein the substrate layer comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

86. A copolymer consisting essentially of resorcinol arylate polyester
5 chain members in combination with C₃₋₂₀ straight chain alkylene, C₃₋₁₀ branched alkylene, or C₄₋₁₀ cyclo- or bicyclo-alkylene chain members, substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method, comprising the steps of :

(a) combining at least one resorcinol moiety and at least one catalyst in a
10 mixture of water and at least one organic solvent substantially immiscible with water;
and

(b) adding to the mixture from (a) at least one dicarboxylic acid dichloride while maintaining the pH between 3 and 8.5 through the presence of an acid acceptor, wherein the total molar amount of acid chloride groups is stoichiometrically deficient
15 relative to the total molar amount of phenolic groups.

87. The copolymer of claim 86, prepared by an interfacial method further comprising the step of : adjusting the pH of the reaction mixture to between 7 and 12 following addition of the at least one dicarboxylic acid dichloride.

88. The copolymer of claim 87, prepared by an interfacial method further
20 comprising the step of : stirring the reaction mixture for at least 3 minutes at pH between 7 and 12.

89. The copolymer of claim 86 wherein the at least one resorcinol moiety is selected from the group consisting of unsubstituted resorcinol, 2-methyl resorcinol, and mixtures thereof.

25 90. The copolymer of claim 89 wherein the at least one resorcinol moiety is unsubstituted resorcinol.

91. The copolymer of claim 86 wherein the at least one dicarboxylic acid dichloride is at least one member selected from the group consisting of isophthaloyl dichloride, terephthaloyl dichloride, naphthalene-2,6-dicarboxylic acid dichloride, sebacyl chloride, cyclohexane-1,4-dicarboxylic acid dichloride and mixtures thereof.
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92. The copolymer of claim 91 wherein the at least one dicarboxylic acid dichloride is a mixture of isophthaloyl dichloride and sebacoyl chloride.
93. The copolymer of claim 92 comprising from about 1 to about 45 mole % sebacate chain members.
- 5 94. The copolymer of claim 86 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.5-1.01 : 1.
95. The copolymer of claim 94 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.2-1.02 : 1.
- 10 96. The copolymer of claim 86 prepared by an interfacial method wherein the pH is maintained using an alkali metal hydroxide, an alkaline earth hydroxide, or an alkaline earth oxide.
97. The copolymer of claim 96 prepared by an interfacial method wherein the pH is maintained using aqueous sodium hydroxide.
- 15 98. The copolymer of claim 86 further comprising at least one chain-stopper selected from the group consisting of mono-phenolic compounds, mono-carboxylic acid chlorides, mono-chloroformates, and mixtures thereof.
99. The copolymer of claim 86 wherein the molecular weight of said copolymer decreases by less than 10% upon heating said polymer at a temperature of about 280-290°C for five minutes.
- 20 100. The copolymer of claim 99 wherein the molecular weight of said copolymer decreases by less than 5% upon heating at a temperature of about 280-290°C for five minutes.
- 25 101. A copolymer consisting essentially of resorcinol arylate polyester chain members in combination with C₁₀ straight chain alkylene or C₆ cycloalkylene chain members, substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by an interfacial method, comprising the steps of :
- 30 (a) combining at least one of unsubstituted resorcinol and 2-methylresorcinol; at least one catalyst selected from the group consisting of quaternary ammonium salts and tertiary amines; and at least one mono-phenolic chain-stopper in a mixture of water and dichloromethane;

(b) adding to the mixture from (a) a mixture comprising at least two members selected from the group consisting of isophthaloyl dichloride, terephthaloyl dichloride, sebacoyl chloride and cyclohexane-1,4-dicarboxylic acid dichloride, while maintaining the pH between 3 and 8.5 through addition of aqueous sodium hydroxide,
5 wherein the ratio of moles total acid chloride groups to moles total phenolic groups is 1.5-1.01 : 1;

(c) adjusting the pH of the reaction mixture to between 8.5 and 10 following addition of the dicarboxylic acid dichloride mixture, and stirring the reaction mixture for at least 3 minutes at said pH; and

10 (d) isolating the copolymer, said copolymer decreasing in molecular weight by less than 10% upon heating at a temperature of about 280-290°C for five minutes.

102. A multilayer article comprising:

a substrate layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and

15 at least one coating layer thereon, said coating layer comprising the copolymer according to claim 86.

103. The article according to claim 102 wherein the substrate comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound

20 104. The article according to claim 103 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

105. The article according to claim 102 wherein the coating layer further comprises at least one colorant.

25 106. The article according to claim 102 wherein the substrate contains at least one of fillers and colorants.

107. The article according to claim 102 further comprising an intermediate layer disposed between said coating and substrate layers.

108. The article according to claim 107 wherein the intermediate layer contains at least one of fillers and colorants.

109. The article according to claim 102 which is an automotive, truck, military vehicle, or motorcycle exterior or interior component, panel, quarter panel, rocker panel, trim, fender, door, decklid, trunklid, hood, bonnet, roof, bumper, fascia, grill, mirror housing, pillar applique, cladding, body side molding, wheel cover, hubcap, door handle, spoiler, window frame, headlamp bezel, headlamp, tail lamp, tail lamp housing, tail lamp bezel, license plate enclosure, roof rack, or running board; an enclosure, housing, panel, part, or trim for an outdoor vehicle or device, an electrical or telecommunication device, network interface device, outdoor furniture, aircraft, boat or marine equipment, outboard motor, depth finder, personal watercraft, jet-ski, pool, spa, hot-tub, step, or step covering, an automatic teller machine (ATM), a lawn or garden tractor, lawn mower, tool, sporting equipment or toy, snowmobile, recreational vehicle, golf course marker, or playground equipment; an enclosure, housing, panel, part, or trim for a computer, desk-top computer, portable computer, lap-top computer, palm-held computer, monitor, printer, keyboard, FAX machine, copier, telephone, mobile phone, radio sender, radio receiver, meter, antenna, light fixture, lighting appliance, transformer, air conditioner; an article used in building or construction, glazing, roofing, window, window trim, floor, wall panel, door, door trim, decorative window furnishing or treatment; a treated glass cover for a picture, painting, poster, or display item; a protected graphic; an outdoor or indoor sign; an article made from a plastic-wood combination; a utility pit cover; cladding or seating for public transportation; cladding or seating for trains, subways, or buses; cladding for satellite dishes; coated helmet or personal protective equipment; coated synthetic or natural textiles; coated photographic film or photographic print; coated painted article; coated dyed article; coated fluorescent article; or coated foam article.

110. A method for preparing a multilayer article which comprises applying at least one thermally stable coating layer to a second layer, said second layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and said coating layer comprising the copolymer according to claim 86.

111. The method according to claim 110 wherein the substrate comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

112. The method according to claim 111 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

113. The method according to claim 110 wherein the coating layer further
5 comprises at least one colorant.

114. The method according to claim 110 wherein the substrate contains at least one of fillers and colorants.

115. The method according to claim 110 further comprising an intermediate layer disposed between said coating and substrate layers.

10 116. The method according to claim 115 wherein the intermediate layer contains at least one of fillers and colorants.

117. The method according to claim 110 wherein said multilayer article is further applied to a substrate layer.

118. The method according to claim 117 wherein the substrate layer
15 comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

119. A block copolymer consisting essentially of resorcinol arylate polyester segments in combination with organic carbonate segments, substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by
20 an interfacial method, comprising the steps of :

(a) combining at least one resorcinol moiety and at least one catalyst in a mixture of water and at least one organic solvent substantially immiscible with water;
and

(b) adding to the mixture from (a) at least one dicarboxylic acid dichloride
25 while maintaining the pH between 3 and 8.5 through the presence of an acid acceptor, wherein the total molar amount of acid chloride groups is stoichiometrically deficient relative to the total molar amount of phenolic groups.

120. The copolymer of claim 119, prepared by an interfacial method further comprising the step of : adjusting the pH of the reaction mixture to between 7 and 12
30 following addition of the at least one dicarboxylic acid dichloride.

121. The copolymer of claim 120, prepared by an interfacial method further comprising the step of : stirring the reaction mixture for at least 3 minutes at pH between 7 and 12.

122. The copolymer of claim 119 wherein the at least one resorcinol moiety
5 is selected from the group consisting of unsubstituted resorcinol, 2-methyl resorcinol, and mixtures thereof.

123. The copolymer of claim 122 wherein the at least one resorcinol moiety is unsubstituted resorcinol.

124. The copolymer of claim 119 wherein the at least one dicarboxylic acid
10 dichloride is at least one member selected from the group consisting of isophthaloyl dichloride, terephthaloyl dichloride, naphthalene-2,6-dicarboxylic acid dichloride, sebacoyl chloride, cyclohexane-1,4-dicarboxylic acid dichloride and mixtures thereof.

125. The copolymer of claim 124 wherein the at least one dicarboxylic acid dichloride is a mixture of isophthaloyl dichloride and terephthaloyl dichloride.

126. The copolymer of claim 125 wherein the ratio of isophthaloyl
15 dichloride to terephthaloyl dichloride is about 0.2-5 : 1.

127. The copolymer of claim 126 wherein the ratio of isophthaloyl dichloride to terephthaloyl dichloride is about 0.8-2.5 : 1.

128. The copolymer of claim 126 wherein the stoichiometric ratio of total
20 phenolic groups to total acid chloride groups is about 1.5-1.01 : 1.

129. The copolymer of claim 128 wherein the stoichiometric ratio of total phenolic groups to total acid chloride groups is about 1.2-1.02 : 1.

130. The copolymer of claim 119 prepared by an interfacial method wherein the pH is maintained using an alkali metal hydroxide, an alkaline earth
25 hydroxide, or an alkaline earth oxide.

131. The copolymer of claim 130 prepared by an interfacial method wherein the pH is maintained using aqueous sodium hydroxide.

132. The copolymer of claim 119 wherein the organic carbonate segments comprise at least one dihydroxy-substituted aromatic hydrocarbon.

133. The copolymer of claim 132 wherein the dihydroxy-substituted aromatic hydrocarbon is bisphenol A.

134. The copolymer of claim 132 further comprising at least one chain-stopper selected from the group consisting of mono-phenolic compounds, mono-
5 carboxylic acid chlorides, mono-chloroformates, and mixtures thereof.

135. The copolymer of claim 119 wherein the molecular weight of said copolymer decreases by less than 12% upon heating said polymer at a temperature of about 280-290°C for five minutes.

136. The copolymer of claim 135 wherein the molecular weight of said
10 copolymer decreases by less than 5% upon heating at a temperature of about 280-290°C for five minutes.

137. A block copolymer consisting essentially of resorcinol arylate polyester segments in combination with organic carbonate segments, substantially free of anhydride linkages linking at least two mers of the polymer chain, prepared by
15 an interfacial method, comprising the steps of :

(a) combining at least one of unsubstituted resorcinol and 2-methylresorcinol; and at least one catalyst selected from the group consisting of quaternary ammonium salts and tertiary amines, in a mixture of water and dichloromethane;

(b) adding to the mixture from (a) a mixture of isophthaloyl dichloride and
20 terephthaloyl dichloride in a molar ratio of isophthalate to terephthalate of 0.4-2.5-1, while maintaining the pH between 3 and 8.5 through addition of aqueous sodium hydroxide, wherein the ratio of moles total acid chloride groups to moles total phenolic groups is 1.5-1.01 : 1;

(c) adjusting the pH of the reaction mixture to between 8.5 and 12 following
25 addition of the dicarboxylic acid dichloride mixture, and stirring the reaction mixture for at least 3 minutes at said pH;

(d) combining the product from (c) with at least one diphenol, at least one mono-phenolic chain-stopper, and phosgene under basic conditions; and

(d) isolating the copolymer, said copolymer decreasing in molecular weight
30 by less than 12% upon heating at a temperature of about 280-290°C for five minutes.

138. A multilayer article comprising:

a substrate layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and

at least one coating layer thereon, said coating layer comprising the copolymer
5 according to claim 119.

139. The article according to claim 138 wherein the substrate comprises at least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound

140. The article according to claim 139 wherein the substrate comprises at
10 least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

141. The article according to claim 138 wherein the coating layer further comprises at least one colorant.

142. The article according to claim 138 wherein the substrate contains at
15 least one of fillers and colorants.

143. The article according to claim 138 further comprising an intermediate layer disposed between said coating and substrate layers.

144. The article according to claim 143 wherein the intermediate layer contains at least one of fillers and colorants.

20 145. The article according to claim 138 which is an automotive, truck, military vehicle, or motorcycle exterior or interior component, panel, quarter panel, rocker panel, trim, fender, door, decklid, trunklid, hood, bonnet, roof, bumper, fascia, grill, mirror housing, pillar applique, cladding, body side molding, wheel cover, hubcap, door handle, spoiler, window frame, headlamp bezel, headlamp, tail lamp,
25 tail lamp housing, tail lamp bezel, license plate enclosure, roof rack, or running board; an enclosure, housing, panel, part, or trim for an outdoor vehicle or device, an electrical or telecommunication device, network interface device, outdoor furniture, aircraft, boat or marine equipment, outboard motor, depth finder, personal water-craft, jet-ski, pool, spa, hot-tub, step, or step covering, an automatic teller machine
30 (ATM), a lawn or garden tractor, lawn mower, tool, sporting equipment or toy,

snowmobile, recreational vehicle, golf course marker, or playground equipment; an enclosure, housing, panel, part, or trim for a computer, desk-top computer, portable computer, lap-top computer, palm-held computer, monitor, printer, keyboard, FAX machine, copier, telephone, mobile phone, radio sender, radio receiver, meter,
5 antenna, light fixture, lighting appliance, transformer, air conditioner; an article used in building or construction, glazing, roofing, window, window trim, floor, wall panel, door, door trim, decorative window furnishing or treatment; a treated glass cover for a picture, painting, poster, or display item; a protected graphic; an outdoor or indoor sign; an article made from a plastic-wood combination; a utility pit cover; cladding or
10 seating for public transportation; cladding or seating for trains, subways, or buses; cladding for satellite dishes; coated helmet or personal protective equipment; coated synthetic or natural textiles; coated photographic film or photographic print; coated painted article; coated dyed article; coated fluorescent article; or coated foam article.

146. A method for preparing a multilayer article which comprises applying
15 at least one thermally stable coating layer to a second layer, said second layer comprising at least one thermoplastic polymer, thermoset polymer, cellulosic material, glass, or metal, and said coating layer comprising the copolymer according to claim 119.

147. The method according to claim 146 wherein the substrate comprises at
20 least one polycarbonate, polyester or addition polymer of an alkenylaromatic compound.

148. The method according to claim 147 wherein the substrate comprises at least one bisphenol A homo- or copolycarbonate, poly(alkylene terephthalate), or ABS or ASA copolymer.

25 149. The method according to claim 146 wherein the coating layer further comprises at least one colorant.

150. The method according to claim 146 wherein the substrate contains at least one of fillers and colorants.

30 151. The method according to claim 146 further comprising an intermediate layer disposed between said coating and substrate layers.

152. The method according to claim 150 wherein the intermediate layer contains at least one of fillers and colorants.

153. The method according to claim 146 wherein said multilayer article is further applied to a substrate layer.

154. The method according to claim 153 wherein the substrate layer comprises at least one polycarbonate, polyester or addition polymer of an
5 alkenylaromatic compound.

INTERNATIONAL SEARCH REPORT

Internat. Application No
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| According to International Patent Classification (IPC) or to both national classification and IPC | | | | |
| B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08G C08J C09D B32B | | | | |
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| Electronic data base consulted during the international search (name of data base and, where practical, search terms used) CHEM ABS Data, EPO-Internal, WPI Data, PAJ | | | | |
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| ° Special categories of cited documents : | | | | |
| <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; border: none; vertical-align: top;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family </td> </tr> </table> | | | "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family |
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| European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo.nl, Fax: (+31-70) 340-3016 | Decocker, L | | | |

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