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(54) Title: METHOD FOR THE OFF-LINE DETERMINATION OF INTRINSIC REACTIVITY OF REACTANTS IN POLY-CONDENSATION REACTIONS

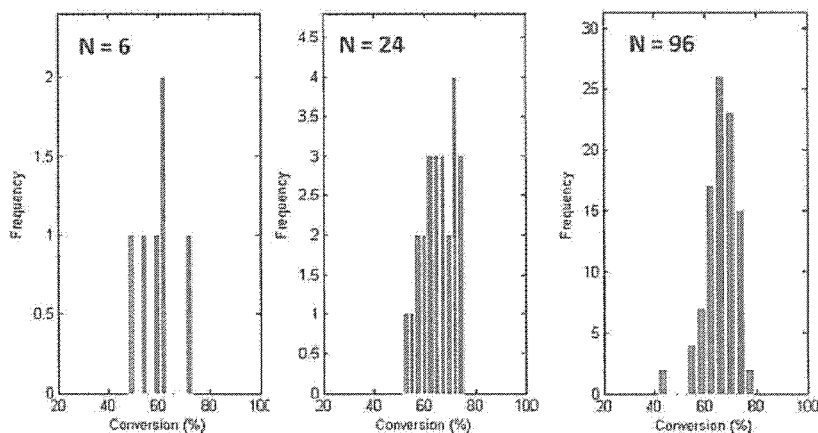


FIG. 1

(57) Abstract: Disclosed herein are methods and systems for determining intrinsic reactivity of polycondensation reactants using near infrared spectroscopy and high throughput screening. This abstract is intended as a scanning tool for purposes of searching in the particular art and is not intended to be limiting of the present invention.

METHOD FOR THE OFF-LINE DETERMINATION OF INTRINSIC REACTIVITY OF REACTANTS IN POLYCONDENSATION REACTIONS

FIELD OF INVENTION

[0001] The present invention relates methods and systems for determining intrinsic reactivity of polycondensation reactants.

BACKGROUND OF THE INVENTION

[0002] In polycondensation reactions, monomers are reacted in the presence of a catalyst, high temperature and vacuum conditions in order to achieve a high molecular weight product. Particularly in polycarbonate manufacture, basic catalysts are employed in concentrations as low as parts per billion with respect to the limiting reagent. Accordingly, the presence of even minute acidic impurities in any of the polycondensation reactants may partially or completely deactivate the catalyst. A full determination of all the potential acidic impurities to these very low levels of concentration and their influence on deactivation kinetics is an impracticable task. Moreover, indirect reactivity tests in practice at many polymerization facilities lack a sufficient level of repeatability and reproducibility to make it useful as a control strategy for a plant production environment. In addition, many reactivity tests require reaction durations in the order of 4 hours, which diminishes its value in corrective actions.

[0003] Accordingly, there remains a need for an indirect measurement of the intrinsic ability of reaction of polycondensation reactants. This and other needs are satisfied by the various aspects of the present disclosure.

SUMMARY OF THE INVENTION

[0004] In one aspect, the invention relates to a method of determining intrinsic reactivity of polycondensation reactants. In various aspects, the invention relates to a method of determining an intrinsic reactivity using near infrared spectroscopy. In various further aspects, the invention relates to a method of determining an intrinsic reactivity using high throughput screening. Thus, in a further aspect, the present methods of determining intrinsic reactivity enable improved measurement accuracy while reducing the required total analysis time.

[0005] In further exemplary aspects, the invention relates to a method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising: providing a plurality of at least substantially identical first polycondensation reaction

mixtures from a single batch of polycondensation reactants; simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product; analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures; determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures.

[0006] In still further exemplary aspects, the invention relates to a system for determining an intrinsic reactivity value of a polycondensation reaction mixture, the system comprising: a reaction unit comprising a plurality of reaction vessels; at least one dispensing unit for dispensing a single batch of polycondensation reactants into each of the plurality of reaction vessels such that each reaction vessel contains a substantially identical first polycondensation reaction mixture; a means for simultaneously subjecting each of the first polycondensation reaction mixtures to conditions effective to result in each first polycondensation reaction mixture forming a second polycondensation reaction mixture comprising a polycondensation product; a means for simultaneously subjecting each of the second polycondensation reaction mixtures to conditions effective to result in termination of the reaction; a near infrared spectrometer unit configured to analyze each second polycondensation reaction mixture and to determine an absorbance spectrum of each second polycondensation reaction mixture; and a computing device unit configured to determine an intrinsic reactivity value of the single batch of polycondensation reactants from the determined absorbance spectrum of each second polycondensation reaction mixture.

[0007] Additional aspects of the invention will be set forth in part in the description which follows, or can be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate exemplary aspects and together with the description, serve to explain the principles of the compositions, methods and systems disclosed herein.

[0009] FIG. 1 is a graph representing the influence of the number of replicates on measurement variability.

[0010] FIG. 2 is a graph representing the quantitative reduction of the confidence interval as a function of the number of replicates.

[0011] FIG. 3 is a graph representing the spectra and BPA calibration curve for samples measured after being dissolved in dichloromethane.

[0012] FIG. 4 is a graph representing the spectra and BPA calibration curve for samples measured without solvent intervention.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

[0014] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0015] Moreover, it is to be understood that unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; and the number or type of embodiments described in the specification.

[0016] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited.

DEFINITIONS

[0017] It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term “comprising” can include the embodiments “consisting of” and “consisting essentially of.” Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined herein.

[0018] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a reaction component” includes mixtures of two or more reaction components.

[0019] As used herein, the term “combination” is inclusive of blends, mixtures, alloys, reaction products, and the like.

[0020] Ranges can be expressed herein as from one particular value, and/or to another particular value. When such a range is expressed, another aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent ‘about,’ it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0021] As used herein, the terms “about” and “at or about” mean that the amount or value in question can be the value designated some other value approximately or about the same. It is generally understood, as used herein, that it is the nominal value indicated $\pm 10\%$ variation unless otherwise indicated or inferred. The term is intended to convey that similar

values promote equivalent results or effects recited in the claims. That is, it is understood that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but can be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. In general, an amount, size, formulation, parameter or other quantity or characteristic is “about” or “approximate” whether or not expressly stated to be such. It is understood that where “about” is used before a quantitative value, the parameter also includes the specific quantitative value itself, unless specifically stated otherwise.

[0022] The terms “first,” “second,” “first part,” “second part,” and the like, where used herein, do not denote any order, quantity, or importance, and are used to distinguish one element from another, unless specifically stated otherwise.

[0023] As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not. For example, the phrase “optionally substituted alkyl” means that the alkyl group can or cannot be substituted and that the description includes both substituted and unsubstituted alkyl groups.

[0024] Disclosed are the components to be used to prepare the systems of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to

all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific aspect or combination of aspects of the methods of the invention.

[0025] References in the specification and concluding claims to parts by weight, of a particular element or component in a composition or article, denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0026] A weight percent ("wt.%") of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included. For example if a particular element or component in a composition or article is said to have 8% by weight, it is understood that this percentage is relative to a total compositional percentage of 100% by weight.

[0027] Compounds are described using standard nomenclature. For example, any position not substituted by any indicated group is understood to have its valence filled by a bond as indicated, or a hydrogen atom. A dash ("-") that is not between two letters or symbols is used to indicate a point of attachment for a substituent. For example, -CHO is attached through carbon of the carbonyl group. Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs.

[0028] The term "alkyl group" as used herein is a branched or unbranched saturated hydrocarbon group of 1 to 24 carbon atoms, such as methyl, ethyl, n propyl, isopropyl, n butyl, isobutyl, t butyl, pentyl, hexyl, heptyl, octyl, decyl, tetradecyl, hexadecyl, eicosyl, tetracosyl and the like. A "lower alkyl" group is an alkyl group containing from one to six carbon atoms.

[0029] The term "aryl group" as used herein is any carbon-based aromatic group including, but not limited to, benzene, naphthalene, etc. The term "aromatic" also includes "heteroaryl group," which is defined as an aromatic group that has at least one heteroatom incorporated within the ring of the aromatic group. Examples of heteroatoms include, but are not limited to, nitrogen, oxygen, sulfur, and phosphorus. The aryl group can be substituted or

unsubstituted. The aryl group can be substituted with one or more groups including, but not limited to, alkyl, alkynyl, alkenyl, aryl, halide, nitro, amino, ester, ketone, aldehyde, hydroxy, carboxylic acid, or alkoxy.

[0030] The term “aralkyl” as used herein is an aryl group having an alkyl, alkynyl, or alkenyl group as defined above attached to the aromatic group. An example of an aralkyl group is a benzyl group.

[0031] The term “carbonate group” as used herein is represented by the formula OC(O)OR, where R can be hydrogen, an alkyl, alkenyl, alkynyl, aryl, aralkyl, cycloalkyl, halogenated alkyl, or heterocycloalkyl group described above.

[0001] As used herein, the terms “number average molecular weight” or “ M_n ” can be used interchangeably, and refer to the statistical average molecular weight of all the polymer chains in the sample and is defined by the formula:

$$M_n = \frac{\sum N_i M_i}{\sum N_i},$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. M_n can be determined for polymers, e.g. polycarbonate polymers, by methods well known to a person having ordinary skill in the art using molecular weight standards, e.g. polycarbonate standards or polystyrene standards, preferably certified or traceable molecular weight standards.

[0032] As used herein, the terms “weight average molecular weight” or “ M_w ” can be used interchangeably, and are defined by the formula:

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i},$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. Compared to M_n , M_w takes into account the molecular weight of a given chain in determining contributions to the molecular weight average. Thus, the greater the molecular weight of a given chain, the more the chain contributes to the M_w . M_w can be determined for polymers, e.g. polycarbonate polymers, by methods well known to a person having ordinary skill in the art using molecular weight standards, e.g. polycarbonate standards or polystyrene standards, preferably certified or traceable molecular weight standards.

[0033] As used herein, “polycarbonate” refers to an oligomer or polymer comprising residues of one or more dihydroxy compounds, e.g. dihydroxy aromatic compounds, joined

by carbonate linkages; it also encompasses homopolycarbonates, copolycarbonates, and (co)polyester carbonates.

[0034] The terms "residues" and "structural units", used in reference to the constituents of the polymers, are synonymous throughout the specification.

[0035] As used herein, the term or phrase "effective," "effective amount," or "conditions effective to" refers to such amount or condition that is capable of performing the function or property for which an effective amount is expressed. As will be pointed out below, the exact amount or particular condition required will vary from one aspect to another, depending on recognized variables such as the materials employed and the processing conditions observed. Thus, it is not always possible to specify an exact "effective amount" or "condition effective to." However, it should be understood that an appropriate effective amount will be readily determined by one of ordinary skill in the art using only routine experimentation.

[0036] Each of the materials disclosed herein are either commercially available and/or the methods for the production thereof are known to those of skill in the art.

[0037] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

METHODS FOR DETERMINING INTRINSIC REACTIVITY

[0038] According to aspects of the disclosure, as briefly described above, the present invention relates to a method for determining intrinsic reactivity of a component in a polycondensation reaction mixture. In various further aspects, the invention relates to a method of determining an intrinsic reactivity using near infrared spectroscopy. In still further aspects, the invention relates to a method of determining an intrinsic reactivity using a high number of replicates. Thus, in yet further aspects, the present methods of determining intrinsic reactivity enable improved measurement accuracy while reducing the required total analysis time.

[0039] In a further aspect, described herein are methods for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising: providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants; simultaneously subjecting the plurality of at least

substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product; analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures; determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures.

[0040] In various aspects, the present invention pertains to polycondensation reaction mixtures. In further aspects, the polycondensation reaction mixtures comprise a first polycondensation reaction mixture, second polycondensation reaction mixture, polycondensation reactant, or polycondensation product, or combinations thereof.

[0041] In a further aspect, the polycondensation reaction mixtures comprise at least one reaction component. In a still further aspect, the reaction component comprises starting reactants, chemical intermediates, reaction by-products, or end products, or combinations thereof. For example, in polycarbonate melt polymerization, the starting reactants can comprise bisphenol A (BPA) or diphenyl carbonate (DPC), the chemical intermediates can comprise oligomers, the reaction by-products can comprise phenol, and the end products can comprise a final polymer.

[0042] In another aspect, the reaction component can be present in any concentration. For example, according to aspects of the disclosure, the reaction component can be present in an amount in the range of from single molecules up to about 100 weight % relative to the total weight of the polycondensation reaction mixture, including further exemplary amounts of about 5 weight %, about 10 weight %, 15 weight %, 20 weight %, 25 weight %, 30 weight %, 35 weight %, 40 weight %, 45 weight %, 50 weight %, 55 weight %, 60 weight %, 65 weight %, 70 weight %, 75 weight %, 80 weight %, 85 weight %, 90 weight %, about 95 weight %. In still further aspects, the reaction component can be present within any range of amount derived from any two of the above stated values. For example, the reaction component can be present in an amount in the range of from about 5 to about 15 weight %, or in an amount in the range of from about 5 weight % to about 20 weight %, or in an amount in

the range of from about 50 weight % to about 85 weight % relative to the total weight of the polycondensation reaction mixture.

[0043] In a further aspect, the polycondensation reaction mixtures comprise individual samples. In a still further aspect, the polycondensation reaction mixtures comprise a plurality of individual polycondensation reaction mixtures. In a yet further aspect, the plurality of polycondensation reaction mixtures comprise an array. In a yet further aspect, the array can comprise a first-order array, a second-order array, or a multi-order array, or combinations thereof.

[0044] In a further aspect, the array may be arranged in a spatially defined array, for example, in a multi-well microtiter plate. In a still further aspect, the multi-well microtiter plate can comprise any number of wells, including, but not limited to 96-well, 192-well, 384-well microtiter plates. Thus, according to aspects of the invention, each of the plurality of polycondensation reaction mixtures is dispensed in and resides in an individual well.

[0045] In a further aspect, each of the plurality of polycondensation reaction mixtures can comprise substantially identical polycondensation reaction mixtures. In a still further aspect, each of the plurality of polycondensation reaction mixtures can comprise different polycondensation reaction mixtures. In a yet further aspect, the plurality of polycondensation reaction mixtures can comprise individual samples, multiple individual samples arranged in a fixed configuration, or a plurality of individual samples.

[0046] According to various aspects of the invention, the polycondensation reaction mixtures are formed from polycondensation reactants. In a further aspect, polycondensation reaction mixtures are formed from a single batch of polycondensation reactants. In a still further aspect, first polycondensation reaction mixtures are formed from a single batch of polycondensation reactants, for example, new polycondensation reactants that have not been previously tested or used.

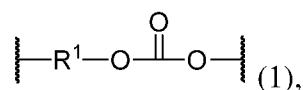
[0047] In one aspect, polycondensation reactants are reacted in the presence of a catalyst, high temperature and vacuum conditions in order to achieve a high molecular weight product. For example, during polycarbonate manufacture, catalysts of a basic nature are involved in very low concentrations (parts per billion range) with respect to the limiting reagent. In this aspect, polycondensation reactants can comprise impurities, and the presence in the polycondensation reactants of minute impurities in concentrations of the same order of magnitude can partially or completely deactivate the catalyst. For example, in previously

untested polycarbonate reactants, the level or amount of impurities is unknown, and impurity influence on deactivation kinetics can be difficult to predict.

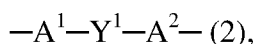
[0048] In a further aspect, the methods comprise second polycondensation reaction mixtures. In a yet further aspect, the second polycondensation reaction mixtures are formed from first polycondensation reaction mixtures. In a still further aspect, the polycondensation reaction mixtures comprise at least one polycondensation product.

[0049] In a further aspect, the polycondensation reaction mixture comprises a polycarbonate reaction mixture. In a still further aspect, the polycarbonate reaction mixture comprises a polycarbonate melt polymerization mixture. In a yet further aspect, the polycondensation product comprises a polycarbonate, a polycarbonate product, or an intermediate polycarbonate product, or combinations thereof.

[0050] In one aspect, a polycarbonate can comprise any polycarbonate material or mixture of materials, for example, as recited in U.S. Patent No. 7,786,246, which is hereby incorporated in its entirety for the specific purpose of disclosing various polycarbonate compositions and methods. The term polycarbonate can be further defined as compositions have repeating structural units of the formula (1):

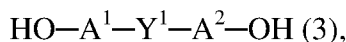


in which at least 60 percent of the total number of R^1 groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Preferably, each R^1 is an aromatic organic radical and, more preferably, a radical of the formula (2):

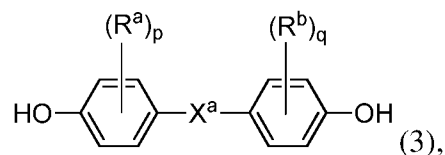


wherein each of A^1 and A^2 is a monocyclic divalent aryl radical and Y^1 is a bridging radical having one or two atoms that separate A^1 from A^2 . In various aspects, one atom separates A^1 from A^2 . For example, radicals of this type include, but are not limited to, radicals such as $-\text{O}-$, $-\text{S}-$, $-\text{S}(\text{O})-$, $-\text{S}(\text{O}_2)-$, $-\text{C}(\text{O})-$, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene. The bridging radical Y^1 is preferably a hydrocarbon group or a saturated hydrocarbon group such as methylene, cyclohexylidene, or isopropylidene.

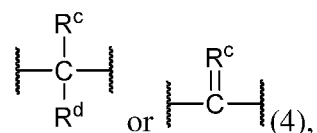
[0051] In a further aspect, polycarbonates can be produced by the reaction of dihydroxy compounds having the formula $\text{HO}-\text{R}^1-\text{OH}$, which includes dihydroxy compounds of formula (3):



wherein Y^1 , A^1 and A^2 are as described above. Also included are bisphenol compounds of general formula (4):



wherein R^a and R^b each represent a halogen atom or a monovalent hydrocarbon group and can be the same or different; p and q are each independently integers from 0 to 4; and X^a represents one of the groups of formula (5):



wherein R^c and R^d each independently represent a hydrogen atom or a monovalent linear or cyclic hydrocarbon group and R^e is a divalent hydrocarbon group.

[0052] In various aspects, examples of suitable dihydroxy compounds include the dihydroxy-substituted hydrocarbons disclosed by name or formula (generic or specific) in U.S. Pat. No. 4,217,438. A nonexclusive list of specific examples of suitable dihydroxy compounds includes the following: resorcinol, 4-bromoresorcinol, hydroquinone, 4,4'-dihydroxybiphenyl, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)diphenylmethane, bis(4-hydroxyphenyl)-1-naphthylmethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2-(4-hydroxyphenyl)-2-(3-hydroxyphenyl)propane, bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 1,1-bis(hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)isobutene, 1,1-bis(4-hydroxyphenyl)cyclododecane, trans-2,3-bis(4-hydroxyphenyl)-2-butene, 2,2-bis(4-hydroxyphenyl)adamantine, (alpha, alpha'-bis(4-hydroxyphenyl)toluene, bis(4-hydroxyphenyl)acetonitrile, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-ethyl-4-hydroxyphenyl)propane, 2,2-bis(3-n-propyl-4-hydroxyphenyl)propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(3-sec-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-t-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 2,2-bis(3-allyl-4-hydroxyphenyl)propane, 2,2-bis(3-methoxy-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dibromo-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dichloro-2,2-bis(5-phenoxy-4-

hydroxyphenyl)ethylene, 4,4'-dihydroxybenzophenone, 3,3-bis(4-hydroxyphenyl)-2-butanone, 1,6-bis(4-hydroxyphenyl)-1,6-hexanedione, ethylene glycol bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)sulfone, 9,9-bis(4-hydroxyphenyl)fluorine, 2,7-dihydroxypyrene, 6,6'-dihydroxy-3,3,3',3'-tetramethylspiro(bis)indane ("spirobiindane bisphenol"), 3,3-bis(4-hydroxyphenyl)phthalide, 2,6-dihydroxydibenzo-p-dioxin, 2,6-dihydroxythianthrene, 2,7-dihydroxyphenoxathin, 2,7-dihydroxy-9,10-dimethylphenazine, 3,6-dihydroxydibenzofuran, 3,6-dihydroxydibenzothiophene, 2,7-dihydroxycarbazole, 3,3-bis(4-hydroxyphenyl)phthalimidine, 2-phenyl-3,3-bis-(4-hydroxyphenyl)phthalimidine (PPPBP), and the like, as well as mixtures including at least one of the foregoing dihydroxy compounds.

[0053] In a further aspect, examples of the types of bisphenol compounds that can be represented by formula (3) includes 1,1-bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (hereinafter "bisphenol A" or "BPA"), 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)octane, 1,1-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl) n-butane, 2,2-bis(4-hydroxy-1-methylphenyl)propane, and 1,1-bis(4-hydroxy-t-butylphenyl)propane. Combinations including at least one of the foregoing dihydroxy compounds can also be used.

[0054] In various aspects, a polycarbonate can employ two or more different dihydroxy compounds or a copolymer of a dihydroxy compounds with a glycol or with a hydroxy- or acid-terminated polyester or with a dibasic acid or hydroxy acid in the event a carbonate copolymer rather than a homopolymer is desired for use. Polyarylates and polyester-carbonate resins or their blends can also be employed. Branched polycarbonates are also useful, as well as blends of linear polycarbonate and a branched polycarbonate. The branched polycarbonates can be prepared by adding a branching agent during polymerization.

[0055] In a further aspect, the branching agents include polyfunctional organic compounds containing at least three functional groups selected from hydroxyl, carboxyl, carboxylic anhydride, haloformyl, and mixtures thereof. Specific examples include trimellitic acid, trimellitic anhydride, trimellitic trichloride, tris-p-hydroxy phenyl ethane, isatin-bis-phenol, tris-phenol TC (1,3,5-tris((p-hydroxyphenyl)isopropyl)benzene), tris-phenol PA (4(4(1,1-bis(p-hydroxyphenyl)-ethyl)alpha, alpha-dimethyl benzyl)phenol), 4-chloroformyl phthalic anhydride, trimesic acid, and benzophenone tetracarboxylic acid. The branching agents can be added at a level of from 0.05-2.0 weight percent. Branching agents and

procedures for making branched polycarbonates are described in U.S. Pat. Nos. 3,635,895 and 4,001,184. All types of polycarbonate end groups are contemplated as being useful in the thermoplastic composition.

[0056] In a further aspect, the polycarbonates are based on bisphenol A, in which each of A¹ and A² is p-phenylene and Y¹ is isopropylidene. In a still further aspect, the molecular weight (Mw) of the polycarbonate is about 10,000 to about 100,000. In a yet further aspect, the polycarbonate has a Mw of about 15,000 to about 55,000. In an even further aspect, the polycarbonate has a Mw of about 18,000 to about 40,000.

[0057] Polycarbonates, including isosorbide-based polyester-polycarbonate, can comprise copolymers comprising carbonate units and other types of polymer units, including ester units, and combinations comprising at least one of homopolycarbonates and copolycarbonates. An exemplary polycarbonate copolymer of this type is a polyester carbonate, also known as a polyester-polycarbonate. Such copolymers further contain carbonate units derived from oligomeric ester-containing dihydroxy compounds (also referred to herein as hydroxy end-capped oligomeric acrylate esters).

[0058] In one aspect, the polycondensation reaction mixtures are subject to conditions effective to result in a formation of polycondensation reaction mixtures comprising a polycondensation product. For example, in a further aspect, the first polycondensation reaction mixtures are subject to conditions effective to result in a formation of second polycondensation reaction mixtures.

[0059] In a further aspect, the polycondensation reaction mixtures are subjected to conditions effective to terminate the reaction. In a still further aspect, all the polycondensation reaction mixtures are simultaneously subjected to conditions effective to terminate the reaction. Depending on the total time before the reaction is terminated, the resulting polycondensation reaction mixture can comprise unreacted starting reactants, chemical intermediates, reaction by-products, or end products, or combinations thereof.

[0060] In some aspects, the polycondensation reaction mixtures are subjected to conditions effective to result in formation of at least one polycarbonate polycondensation product. In a further aspect, conditions effective comprise reaction conditions of a melt polymerization reaction, for example, reaction conditions and components involved in the melt polymerization of polycarbonates. Generally, in the melt polymerization process, polycarbonates are prepared by co-reacting, in a molten state, the dihydroxy reactant(s) (i.e., isosorbide, aliphatic diol and/or aliphatic diacid, and any additional dihydroxy compound)

and a diaryl carbonate ester, such as diphenyl carbonate, or more specifically in an aspect, an activated carbonate such as bis(methyl salicyl)carbonate, in the presence of a transesterification catalyst. The reaction can be carried out in typical polymerization equipment, such as one or more continuously stirred reactors (CSTRs), plug flow reactors, wire wetting fall polymerizers, free fall polymerizers, wiped film polymerizers, BANBURY® mixers, single or twin screw extruders, or combinations of the foregoing. In one aspect, volatile monohydric phenol can be removed from the molten reactants by distillation and the polymer is isolated as a molten residue.

[0061] In a further aspect, the melt polymerization can include a transesterification catalyst comprising a first catalyst, also referred to herein as an alpha catalyst, comprising a metal cation and an anion. In an aspect, the cation is an alkali or alkaline earth metal comprising Li, Na, K, Cs, Rb, Mg, Ca, Ba, Sr, or a combination comprising at least one of the foregoing. The anion is hydroxide (OH^-), superoxide (O^{2-}), thiolate (HS^-), sulfide (S^{2-}), a C_{1-20} alkoxide, a C_{6-20} aryloxy, a C_{1-20} carboxylate, a phosphate including biphosphate, a C_{1-20} phosphonate, a sulfate including bisulfate, sulfites including bisulfites and metabisulfites, a C_{1-20} sulfonate, a carbonate including bicarbonate, or a combination comprising at least one of the foregoing. In another aspect, salts of an organic acid comprising both alkaline earth metal ions and alkali metal ions can also be used. Salts of organic acids useful as catalysts are illustrated by alkali metal and alkaline earth metal salts of formic acid, acetic acid, stearic acid and ethylenediaminetetraacetic acid. The catalyst can also comprise the salt of a non-volatile inorganic acid. By "nonvolatile", it is meant that the referenced compounds have no appreciable vapor pressure at ambient temperature and pressure. In particular, these compounds are not volatile at temperatures at which melt polymerizations of polycarbonate are typically conducted. The salts of nonvolatile acids are alkali metal salts of phosphites; alkaline earth metal salts of phosphites; alkali metal salts of phosphates; and alkaline earth metal salts of phosphates. Exemplary transesterification catalysts include, lithium hydroxide, sodium hydroxide, potassium hydroxide, cesium hydroxide, magnesium hydroxide, calcium hydroxide, barium hydroxide, lithium formate, sodium formate, potassium formate, cesium formate, lithium acetate, sodium acetate, potassium acetate, lithium carbonate, sodium carbonate, potassium carbonate, lithium methoxide, sodium methoxide, potassium methoxide, lithium ethoxide, sodium ethoxide, potassium ethoxide, lithium phenoxide, sodium phenoxide, potassium phenoxide, sodium sulfate, potassium sulfate, NaH_2PO_3 , NaH_2PO_4 , $\text{Na}_2\text{H}_2\text{PO}_3$, KH_2PO_4 , CsH_2PO_4 , $\text{Cs}_2\text{H}_2\text{PO}_4$, Na_2SO_3 , $\text{Na}_2\text{S}_2\text{O}_5$, sodium mesylate,

potassium mesylate, sodium tosylate, potassium tosylate, magnesium disodium ethylenediamine tetraacetate (EDTA magnesium disodium salt), or a combination comprising at least one of the foregoing. It will be understood that the foregoing list is exemplary and should not be considered as limited thereto. In one aspect, the transesterification catalyst is an alpha catalyst comprising an alkali or alkaline earth salt. In an exemplary aspect, the transesterification catalyst comprises sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, sodium methoxide, potassium methoxide, NaH_2PO_4 , or a combination comprising at least one of the foregoing.

[0062] The amount of alpha catalyst can vary widely according to the conditions of the melt polymerization, and can be about 0.001 to about 500 micromoles (μmol). In an aspect, the amount of alpha catalyst can be about 0.01 to about 20 μmol , specifically about 0.1 to about 10 μmol , more specifically about 0.5 to about 9 μmol , and still more specifically about 1 to about 7 μmol , per mole of aliphatic diol and any other dihydroxy compound present in the melt polymerization.

[0063] In another aspect, a second transesterification catalyst, also referred to herein as a beta catalyst, can optionally be included in the melt polymerization process, provided that the inclusion of such a second transesterification catalyst does not significantly adversely affect the desirable properties of the polycarbonate. Exemplary transesterification catalysts can further include a combination of a phase transfer catalyst of formula $(\text{R}^3)_4\text{Q}^+\text{X}$ above, wherein each R^3 is the same or different, and is a C_{1-10} alkyl group; Q is a nitrogen or phosphorus atom; and X is a halogen atom or a C_{1-8} alkoxy group or C_{6-18} aryloxy group. Exemplary phase transfer catalyst salts include, for example, $[\text{CH}_3(\text{CH}_2)_3]_4\text{NX}$, $[\text{CH}_3(\text{CH}_2)_3]_4\text{PX}$, $[\text{CH}_3(\text{CH}_2)_5]_4\text{NX}$, $[\text{CH}_3(\text{CH}_2)_6]_4\text{NX}$, $[\text{CH}_3(\text{CH}_2)_4]_4\text{NX}$, $\text{CH}_3[\text{CH}_3(\text{CH}_2)_3]_3\text{NX}$, and $\text{CH}_3[\text{CH}_3(\text{CH}_2)_2]_3\text{NX}$, wherein X is Cl^- , Br^- , a C_{1-8} alkoxy group or a C_{6-18} aryloxy group. Examples of such transesterification catalysts include tetrabutylammonium hydroxide, methyltributylammonium hydroxide, tetrabutylammonium acetate, tetrabutylphosphonium hydroxide, tetrabutylphosphonium acetate, tetrabutylphosphonium phenolate, or a combination comprising at least one of the foregoing. Other melt transesterification catalysts include alkaline earth metal salts or alkali metal salts. In various aspects, where a beta catalyst is desired, the beta catalyst can be present in a molar ratio, relative to the alpha catalyst, of less than or equal to 10, specifically less than or equal to 5, more specifically less than or equal to 1, and still more specifically less than or equal to 0.5. In other aspects, the melt polymerization reaction disclosed herein uses only an alpha

catalyst as described hereinabove, and is substantially free of any beta catalyst. As defined herein, “substantially free of” can mean where the beta catalyst has been excluded from the melt polymerization reaction. In one aspect, the beta catalyst is present in an amount of less than about 10 parts per million (ppm), specifically less than 1 ppm, more specifically less than about 0.1 ppm, more specifically less than or equal to about 0.01 ppm, and more specifically less than or equal to about 0.001 ppm, based on the total weight of all components used in the melt polymerization reaction.

[0064] In one aspect, an end-capping agent (also referred to as a chain-stopper) can optionally be used to limit molecular weight growth rate, and so control molecular weight in the polycarbonate. Exemplary chain-stoppers include certain monophenolic compounds (i.e., phenyl compounds having a single free hydroxy group), monocarboxylic acid chlorides, and/or monochloroformates. Phenolic chain-stoppers are exemplified by phenol and C₁-C₂₂ alkyl-substituted phenols such as p-cumyl-phenol, resorcinol monobenzoate, and p- and tertiary-butyl phenol, cresol, and monoethers of diphenols, such as p-methoxyphenol. Alkyl-substituted phenols with branched chain alkyl substituents having 8 to 9 carbon atoms can be specifically mentioned.

[0065] In another aspect, endgroups can be derived from the carbonyl source (i.e., the diaryl carbonate), from selection of monomer ratios, incomplete polymerization, chain scission, and the like, as well as any added end-capping groups, and can include derivatizable functional groups such as hydroxy groups, carboxylic acid groups, or the like. In one aspect, the endgroup of a polycarbonate, including a polycarbonate polymer as defined herein, can comprise a structural unit derived from a diaryl carbonate, where the structural unit can be an endgroup. In a further aspect, the endgroup is derived from an activated carbonate. Such endgroups can be derived from the transesterification reaction of the alkyl ester of an appropriately substituted activated carbonate, with a hydroxy group at the end of a polycarbonate polymer chain, under conditions in which the hydroxy group reacts with the ester carbonyl from the activated carbonate, instead of with the carbonate carbonyl of the activated carbonate. In this way, structural units derived from ester containing compounds or substructures derived from the activated carbonate and present in the melt polymerization reaction can form ester endgroups.

[0066] In one aspect, the melt polymerization reaction can be conducted by subjecting the polycondensation reaction mixtures to a series of temperature-pressure-time protocols. In some aspects, this involves gradually raising the reaction temperature in stages while

gradually lowering the pressure in stages. In one aspect, the pressure is reduced from about atmospheric pressure at the start of the reaction to about 1 millibar (100 Pascals (Pa)) or lower, or in another aspect to 0.1 millibar (10 Pa) or lower in several steps as the reaction approaches completion. The temperature can be varied in a stepwise fashion beginning at a temperature of about the melting temperature of the polycondensation reaction mixture and subsequently increased to final temperature. In one aspect, the polycondensation reaction mixture is heated from room temperature to about 150 °C. In such an aspect, the polymerization reaction starts at a temperature of about 150 °C to about 220 °C. In another aspect, the polymerization temperature can be up to about 220 °C. In other aspects, the polymerization reaction can then be increased to about 250 °C and then optionally further increased to a temperature of about 320 °C, and all subranges there between.

[0067] In another aspect, the total reaction time can be from about 30 minutes to about 360 minutes and all subranges there between. This procedure will generally ensure that the reactants react to give polycarbonates with the desired molecular weight, glass transition temperature and physical properties. The reaction proceeds to build the polycarbonate chain with production of ester-substituted alcohol by-product such as methyl salicylate. In one aspect, efficient removal of the by-product can be achieved by different techniques such as reducing the pressure. Generally the pressure starts relatively high in the beginning of the reaction and is lowered progressively throughout the reaction and temperature is raised throughout the reaction. After the desired melt viscosity and/or molecular weight is reached, the final polycarbonate product can be isolated from the reactor in a solid or molten form.

[0068] In various aspects, the disclosed methods comprise analyzing a plurality of polycondensation reaction mixtures or reaction components. In one aspect, each of the plurality of individual polycondensation reaction mixtures is analyzed substantially simultaneously. In another aspect, each of the plurality of individual polycondensation reaction mixtures is analyzed separately.

[0069] In a further aspect, the disclosed methods comprise analyzing the polycondensation reaction mixtures or reaction components using near-infrared spectroscopy (NIR). In a still further aspect, near infrared spectroscopy is used to determine an absorbance spectrum of the polycondensation reaction mixtures or reaction components.

[0070] In one aspect, near-infrared spectroscopy (NIR) is an analytical method that uses the near-infrared region of the electromagnetic spectrum (from about 800 nanometers (nm) to 2500 nm) for qualitative or quantitative chemical analysis. The NIR molecular

overtones and combined absorption bands are typically very broad, leading to complex spectra and making difficult to assign specific features to specific chemical components.

[0071] In a further aspect, the measured absorbance spectrum comprises at least one wavelength in the range from about 800 nm to 2500 nm. In a still further aspect, the measured absorbance spectrum comprises at least one wavelength in the range from about 1500 nm to 2000 nm. In a yet further aspect, the absorbance spectrum comprises multiple wavelengths. In an even further aspect, the absorbance spectrum comprises at least one entire absorption band.

[0072] In various aspects, the disclosed methods comprise application of mathematical analysis techniques to extract the desired chemical information from the absorbance spectrum data.

[0073] In an aspect, one wavelength is used to determine a concentration of one or more reaction components. When one wavelength is used, concentrations of reaction components are determined using mathematical analysis techniques comprising univariate analysis. In a further aspect, multiple wavelengths are used to determine a concentration of one or more reaction components. When multiple wavelengths are used, reaction component concentrations are determined using mathematical analysis techniques comprising multivariate analysis.

[0074] In a further aspect, multivariate analysis comprises principal components analysis, partial least squares analysis, artificial neural networks analysis, linear multivariate analysis, or nonlinear multivariate analysis.

[0075] In a further aspect, one or more steps involved in determining the concentration of reaction components are performed using computer software. In a still further aspect, the computer software can comprise any computer software suitable for use in performing calculations employed in determining concentrations of reaction components. Non-limiting examples of computer software include MATLAB, TQ Analyst Quantification Software, and MINITAB.

[0076] Thus, in further aspects, analyzing comprises irradiating each of the plurality of individual polycondensation reaction mixtures with at least one wavelength of near infrared radiation and measuring the absorbance spectrum of each of the plurality of individual polycondensation reaction mixtures, and correlating absorbance values to concentrations of a reaction component.

[0077] In various aspects, the disclosed methods comprise determining an intrinsic reactivity of polycondensation reactants. In a further aspect, the polycondensation reactions comprise a single batch of polycondensation reactants. In a still further aspect, the intrinsic reactivity is determined using the calculated concentration of the one or more components present in a polycondensation reaction mixture, for example, using the concentration of one or more components present in each of the plurality of the second polycondensation reaction mixtures.

[0078] In a further aspect, the intrinsic reactivity is determined by comparing the degree of conversion exhibited by a polycondensation reactant with the degree of conversion of a known reference sample tested in substantially the same reaction conditions.

[0079] In a further aspect, the intrinsic reactivity is used to determine deactivation kinetics of previously untested polycondensation reactants. In a still further aspect, the intrinsic reactivity permits determination of the effect on reactivity from impurities formed from the untested polycondensation reactants during the polycondensation reaction. In a yet further aspect, the intrinsic reactivity values can thus be used to determine the correction factor needed to overcome impurity influence on deactivation kinetics. For example, in some aspects, the correction factor can comprise adjustment in the amount of catalyst added to the polycondensation reaction mixtures.

SYSTEMS FOR DETERMINING INTRINSIC REACTIVITY

[0080] According to other aspects, the present invention also relates to a system for determining an intrinsic reactivity value of a polycondensation reaction mixture, the system comprising: a reaction unit comprising a plurality of reaction vessels; at least one dispensing unit for dispensing a single batch of polycondensation reactants into each of the plurality of reaction vessels such that each reaction vessel contains a substantially identical first polycondensation reaction mixture; a means for simultaneously subjecting each of the first polycondensation reaction mixtures to conditions effective to result in each first polycondensation reaction mixture forming a second polycondensation reaction mixture comprising a polycondensation product; a means for simultaneously subjecting each of the second polycondensation reaction mixtures to conditions effective to result in termination of the reaction; a near infrared spectrometer unit configured to analyze each second polycondensation reaction mixture and to determine an absorbance spectrum of each second polycondensation reaction mixture; and a computing device unit configured to determine an

intrinsic reactivity value of the single batch of polycondensation reactants from the determined absorbance spectrum of each second polycondensation reaction mixture.

[0081] In one aspect, the reaction unit comprises individual reaction vessels. In a further aspect, the reaction unit comprises a plurality of individual reaction vessels. In a still further aspect, the reaction vessels comprise glass or quartz vials.

[0082] In a further aspect, the reaction unit comprises an array. In a still further aspect, the array can comprise a first-order array, a second-order array, or a multi-order array, or combinations thereof. In a yet further aspect, the array may be arranged in a spatially defined array, for example, in a multi-well or multi-vessel microtiter plate. In an even further aspect, the microtiter plate can comprise any number of wells or vessels, including, but not limited to 96-well, 192-well, 384-well microtiter plates. Thus, according to aspects of the invention, each of the plurality of polycondensation reaction mixtures is dispensed in and reside in an individual reaction vessel.

[0083] In another aspect, the system comprises at least one dispensing unit for metering, dosing, and dispensing of the polycondensation reactants. In a further aspect, the dispensing unit comprises a gravimetric dispensing system or a volumetric dispensing system. In a still further aspect, the polycondensation reactants are dispensed in the reaction vessels simultaneously or successively.

[0084] In various aspects, the system comprises a means for controlling the reaction conditions of the reaction unit, for example, by controlling temperature or pressure. In one aspect, the system comprises a means for subjecting polycondensation reaction mixtures to conditions effective to result in a formation of polycondensation reaction mixtures comprising a polycondensation product, for example, a means for controlling temperature or pressure. In a further aspect, the first polycondensation reaction mixtures are subject to conditions effective to result in a formation of second polycondensation reaction mixtures.

[0085] In a further aspect, the system comprises a means for subjecting polycondensation reaction mixtures to conditions effective to terminate the reaction, for example, using a means for controlling temperature or pressure. In some aspects, conditions effective to terminate the reaction comprise fast cooling the mixture, for example, to a temperature below which kinetics are inhibited. In other aspects, conditions effective to terminate the reaction comprise adding a chemical capable of neutralizing the catalyst. In still further aspects, conditions effective to terminate the reaction comprises adding a chemical

capable of reacting with a chain ends to produce a new chain which is chemically incapable of further growth.

[0086] In a still further aspect, all the polycondensation reaction mixtures are simultaneously subjected to same reaction conditions. In a yet further aspect, all the polycondensation reaction mixtures are simultaneously subjected to conditions effective to terminate the reaction. Depending on the total reaction time, the resulting polycondensation reaction mixture can comprise unreacted starting reactants, chemical intermediates, reaction by-products, or end products, or combinations thereof.

[0087] In a further aspect, the means for controlling temperature or pressure comprise a temperature control unit or a pressure control unit, respectively. In a still further aspect, the temperature control unit comprises a heating unit, or a cooling unit, or a combination thereof.

[0088] In another aspect, the means for subjecting the polycondensation reaction mixtures to conditions effective results in formation of at least one polycarbonate polycondensation product. In a further aspect, conditions effective comprise reaction conditions of a melt polymerization reaction, for example, reaction conditions and components involved in the melt polymerization of polycarbonates.

[0089] In a further aspect, the means for subjecting to conditions effective comprises an admixing unit. In this aspect, the admixing unit shakes or agitates the reaction unit or reaction vessels to cause mixing of the polycondensation reactants and formation of a polycondensation reaction mixture.

[0090] In a further aspect, the admixing unit comprises a means for stirring the plurality of polycondensation reaction mixtures. In a still further aspect, the means for stirring comprises a plurality of stirring instruments. In a yet further aspect, each of the plurality of stirring instruments corresponds to a reaction vessel.

[0091] In another aspect, the means for subjecting to conditions effective comprise a temperature control unit. In a further aspect, the temperature control unit comprises a heating unit, or a cooling unit, or a combination thereof.

[0092] In a further aspect, the heating unit comprises a heating element. Non-limiting examples of suitable heating element include heat plates, heat lamps, and heating baths using suitable heat transfer media, for example, using hot water, hot oil, or fluidized sand.

[0093] In a further aspect, the cooling unit comprises a cooling element. The cooling element can comprise any cooling element suitable for use in terminating a reaction. Non-limiting examples of cooling elements include refrigerated baths using cooling transfer

media, for example, using chilled water, brine, Freon, ammonia or sublimating solid carbon dioxide.

[0094] In other aspects, the system comprises a near infrared spectrometer unit configured to analyze the polycondensation reaction mixtures. In one aspect, the near infrared spectrometer unit is configured to analyze a single reaction vessel. In a further aspect, the near infrared spectrometer unit is configured to analyze a plurality of reaction vessels. In still a further aspect, the NIR spectrometer unit is configured to analyze the plurality of reaction vessels simultaneously or in parallel. In some aspects, the system comprises a Raman spectrometer unit configured to analyze the polycondensation reaction mixtures. In other aspects, the system comprises a UV-Vis spectrometer unit configured to analyze the polycondensation reaction mixtures.

[0095] In further aspects, the NIR unit is configured to determine absorbance spectrum or spectroscopic data which are evaluated as described herein. In one aspect, the absorbance spectrum measured by the NIR spectrometer unit comprises at least one wavelength in the range of from 800 nm to 2500 nm. In a further aspect, the absorbance spectrum comprises at least one wavelength in the range of from 1500 nm to 2000 nm.

[0096] In other aspects, the absorbance spectrum comprises multiple wavelengths. In still further aspects, the absorbance spectrum comprises an entire absorption band.

[0097] In another aspect, the NIR spectrometer unit is configured to irradiate each of the plurality of individual polycondensation reaction mixtures with at least one wavelength of near infrared radiation and configured to determine the absorbance spectrum of each of the plurality of individual polycondensation reaction mixtures.

[0098] In various aspects, the system comprises a computing device unit configured to receive the determined absorbance spectrum data from the NIR spectroscopic unit. In further aspects, the computing device unit is configured to perform mathematical analysis of the determined absorbance spectrum to extract chemical information. In still further aspects, the chemical information comprises the concentration of at least one reaction component present in a polycondensation reaction mixture. Thus, in other aspects, the mathematical analysis comprises determining the concentration of at least one reaction component using the determined absorbance spectrum.

[0099] In another aspect, the computing device unit comprises computing hardware and software for performing mathematical analysis of the absorbance spectrum to extract

chemical information. In a further aspect, the software performs one or more steps relating to application of mathematical analysis techniques to extract chemical information.

[00100] In a further aspect, the software can comprise any computer software suitable for use in performing calculations employed in determining concentrations of reaction components. Non-limiting examples of computer software include MATLAB, TQ Analyst Quantification Software, and MINITAB.

[00101] In some aspects, the computing device unit uses one wavelength of the absorbance spectrum to determine a concentration of at least one reaction component. In further aspects, determining the concentration of at least one reaction component using one wavelength comprises univariate analysis.

[00102] In other aspects, the computing device unit uses multiple wavelengths to determine the concentration of at least one reaction component. In yet further aspects, determining the concentration of at least one reaction components comprises multivariate analysis. In still further aspects, multivariate analysis comprises neural networks analysis, principal components analysis, partial least squares analysis, linear multivariate analysis, or nonlinear multivariate analysis.

[00103] In further aspects, the computing device unit determines an intrinsic reactivity value by comparing the degree of conversion exhibited by a polycondensation reactant with the degree of conversion of a known reference sample tested in substantially the same reaction conditions.

[00104] In other aspects, the system parts or steps can be manual or automated. In one aspect, at least a portion of system parts or steps are electrically driven. In a further aspect, at least a portion of the system parts or steps are performed by a robotic device.

[00105] In various further aspects, the present methods and system provide advantages over standard reactivity tests of the prior art. For example, one drawback of standard reactivity tests is their accuracy. To this end, standard reactivity tests lack the requisite repeatability and reproducibility needed to make it a useful aspect in control strategies of polycondensation reactions. Another drawback to standard reactivity test is its high duration of reaction, which in various aspects, diminishes any value it has in taking corrective actions in a polycondensation plant environment.

[00106] In one aspect, the disclosed methods and systems provide improved measurement accuracy while reducing the total analysis time. In a further aspect, the disclosed methods and systems exhibit a Gage Repeatability and Reproducibility (GRR) of

less than or equal to 30%. In a still further aspect, the Gage Repeatability and Reproducibility (GRR) is less than or equal to 25%.

[00107] Because of the high number of replicates, the disclosed methods and systems exhibit improved influence on confidence intervals. In one aspect, the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 95%. In a further aspect, the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 98%.

[00108] In various aspects, the present invention pertains to and includes at least the following aspects.

[00109] Aspect 1: A method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising: a) providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants; b) simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product; c) analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures; d) determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and e) determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures.

[00110] Aspect 2: The method of aspect 1, wherein the polycondensation reaction mixture comprises a polycarbonate polymerization reaction mixture.

[00111] Aspect 3: The method of any preceding aspect, wherein the reaction component comprises starting reactants, chemical intermediates, reaction by-products, or end products, or combinations thereof.

[00112] Aspect 4: The method according to any preceding aspect, wherein the reaction component comprises bisphenol A, diphenyl carbonate, an oligomer, phenol, or a polycarbonate polymer, or combinations thereof.

[00113] Aspect 5: The method according to any preceding aspect, wherein the reaction component is present in an amount from greater than 0 weight% to 100 weight % of polycondensation reaction mixture.

[00114] Aspect 6: The method according to any preceding aspect, wherein the reaction component comprises DPC.

[00115] Aspect :7 The method according to any preceding aspect, wherein the reaction component comprises BPA.

[00116] Aspect 8: The method according to any preceding aspect, wherein the reaction component comprises phenol.

[00117] Aspect 9: The method according to any preceding aspect, wherein the polycondensation reactants comprise an aromatic dihydroxy compound or a diaryl carbonate ester.

[00118] Aspect 10: The method according to any preceding aspect, wherein the polycondensation reactants comprise bisphenol A (BPA) or diphenyl carbonate (DPC).

[00119] Aspect 11: The method according to any preceding aspect, wherein conditions effective comprise reaction conditions of a melt polymerization reaction.

[00120] Aspect 12: The method according to any preceding aspect, wherein the plurality of reaction mixtures comprises an array.

[00121] Aspect 13: The method according to any preceding aspect, wherein the plurality of reaction mixtures comprises a first-order array.

[00122] Aspect 14: The method according to any preceding aspect, wherein the plurality of reaction mixtures comprises a second-order or higher array.

[00123] Aspect 15: The method according to any preceding aspect, wherein the plurality of reaction mixtures comprises a multi-order array.

[00124] Aspect 16: The method according to any preceding aspect, wherein the plurality of reaction mixtures comprise a multi-well microtiter plate.

[00125] Aspect 17: The method according to any preceding aspect, wherein the plurality of reaction mixtures comprise individual samples, multiple individual samples arranged in a fixed configuration, or a plurality of individual samples.

[00126] Aspect 18: The method according to any preceding aspect, wherein analyzing each of the plurality of individual polycondensation reaction mixtures is substantially simultaneous.

[00127] Aspect 19: The method according to any preceding aspect, wherein analyzing each of the plurality of individual polycondensation reaction mixtures is separate.

[00128] Aspect 20: The method according to any preceding aspect, further comprising simultaneously subjecting the plurality of the second polycondensation reaction mixtures to conditions effective to terminate the reaction.

[00129] Aspect 21: The method according to any preceding aspect, wherein the polycondensation product comprises a polycarbonate product or intermediate polycarbonate product.

[00130] Aspect 22: The method according to any preceding aspect, wherein analyzing comprises irradiating each of the plurality of individual polycondensation reaction mixtures with at least one wavelength of near infrared radiation and measuring the absorbance spectrum of each of the plurality of individual polycondensation reaction mixtures, and correlating absorbance values to levels of a reaction component.

[00131] Aspect 23: The method according to any preceding aspect, wherein absorbance spectrum comprises at least one wavelength in the range of from 800 nm to 2500 nm.

[00132] Aspect 24: The method according to any preceding aspect, wherein absorbance spectrum comprises at least one wavelength in the range of from 1500 nm to 2000 nm.

[00133] Aspect 25: The method according to any preceding aspect, wherein absorbance spectrum comprises multiple wavelengths.

[00134] Aspect 26: The method according to any preceding aspect, wherein absorbance spectrum comprises an entire absorption band.

[00135] Aspect 27: The method according to any preceding aspect, wherein one wavelength is used to determine a concentration of one or more reaction components.

[00136] Aspect 28: The method according to any preceding aspect, wherein determining a concentration of one or more reaction components comprises univariate analysis.

[00137] Aspect 29: The method according to any preceding aspect, wherein multiple wavelengths are used to determine a concentration of one or more reaction components.

[00138] Aspect 30: The method according to any preceding aspect, wherein determining a concentration of one or more reaction components comprises multivariate analysis.

[00139] Aspect 31: The method according to any preceding aspect, wherein multivariate analysis comprises neural networks analysis, principal components analysis, partial least squares analysis, linear multivariate analysis, or nonlinear multivariate analysis.

[00140] Aspect 32: The method according to any preceding aspect, wherein at least one step in determining a concentration of one or more reaction components is performed using computer software.

[00141] Aspect 33: The method according to any preceding aspect, wherein determining an intrinsic reactivity comprises comparing the degree of conversion exhibited by a polycondensation reactant with the degree of conversion of a known reference sample tested in substantially the same reaction conditions.

[00142] Aspect 34: The method according to any preceding aspect, wherein the intrinsic reactivity is used to determine deactivation kinetics of the polycondensation reaction mixture.

[00143] Aspect 35: The method according to any preceding aspect, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 30%.

[00144] Aspect 36: The method according to any preceding aspect, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 25%.

[00145] Aspect 37: The method according to any preceding aspect, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 95%.

[00146] Aspect 38: The method according to any preceding aspect, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 98%.

[00147] Aspect 39: A method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising: a) providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants; b) simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product; c) simultaneously subjecting the plurality of the second polycondensation reaction mixtures to conditions effective to terminate the reaction; d) analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second

polycondensation reaction mixtures; e) determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and f) determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures.

[00148] Aspect 40: A method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising: a) providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants comprising bisphenol A (BPA) and diphenyl carbonate (DPC); b) simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product; c) analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures; d) determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and e) determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures; wherein the components comprise BPA, DPC, phenol, or combinations thereof.

[00149] Aspect 41: A system for determining an intrinsic reactivity value of a polycondensation reaction mixture, the system comprising: a) a reaction unit comprising a plurality of reaction vessels; b) at least one dispensing unit for dispensing a single batch of polycondensation reactants into each of the plurality of reaction vessels such that each reaction vessel contains a substantially identical first polycondensation reaction mixture; c) a means for simultaneously subjecting each of the first polycondensation reaction mixtures to conditions effective to result in each first polycondensation reaction mixture forming a second polycondensation reaction mixture comprising a polycondensation product; d) a means for simultaneously subjecting each of the second polycondensation reaction mixtures to conditions effective to result in termination of the reaction; e) a near infrared spectrometer unit configured to analyze each second polycondensation reaction mixture and to determine an absorbance spectrum of each second polycondensation reaction mixture; and f) a

computing device unit configured to determine an intrinsic reactivity value of the single batch of polycondensation reactants from the determined absorbance spectrum of each second polycondensation reaction mixture.

[00150] Aspect 42: The system of aspect 41, wherein the reaction unit comprises individual reaction vessels, multiple individual vessels arranged in a fixed configuration, or a plurality of individual vessels.

[00151] Aspect 43: The system according to any preceding aspect, wherein the reaction unit comprises an array.

[00152] Aspect 44: The system according to any preceding aspect, wherein the reaction unit comprises a first-order array, a second-order array, or a multi-order array, or combinations thereof.

[00153] Aspect 45: The system according to any preceding aspect, wherein the reaction unit comprises a multi-well microtiter plate.

[00154] Aspect 46: The system according to any preceding aspect, wherein the multi-well microtiter plate comprises a 96-well, 192-well, or 384-well microtiter plate.

[00155] Aspect 47: The system according to any preceding aspect, wherein the reaction vessels comprise glass or quartz vials.

[00156] Aspect 48: The system according to any preceding aspect, wherein the dispensing unit comprises a gravimetric dispensing system or a volumetric dispensing system.

[00157] Aspect 49: The system according to any preceding aspect, wherein the polycondensation reactants are dispensed in the reaction vessels simultaneously or successively.

[00158] Aspect 50: The system according to any preceding aspect, wherein the means for simultaneously subjecting to conditions effective comprises an admixing unit.

[00159] Aspect 51: The system according to any preceding aspect, wherein the admixing unit shakes or agitates the reaction unit or reaction vessels to cause mixing of the polycondensation reactants.

[00160] Aspect 52: The system according to any preceding aspect, wherein the admixing unit comprises a means for stirring the plurality of polycondensation reaction mixtures.

[00161] Aspect 53: The system according to any preceding aspect, wherein the means for stirring comprises a plurality of stirring instruments.

[00162] Aspect 54: The system according to any preceding aspect, wherein each of the plurality of stirring instruments corresponds to a reaction vessel.

[00163] Aspect 55: The system according to any preceding aspect, wherein the means for simultaneously subjecting conditions effective comprise a temperature control unit.

[00164] Aspect 56: The system according to any preceding aspect, wherein the temperature control unit comprises a heating unit, or a cooling unit, or a combination thereof.

[00165] Aspect 57: The system according to any preceding aspect, wherein the heating unit comprises a heating element.

[00166] Aspect 58: The system according to any preceding aspect, wherein the heating element comprises a heat plate, heat lamp, or heating bath.

[00167] Aspect 59: The system according to any preceding aspect, the cooling unit comprises a cooling element.

[00168] Aspect 60: The system according to any preceding aspect, wherein the cooling element comprises a refrigerated bath.

[00169] Aspect 61: The system according to any preceding aspect, wherein the near infrared spectrometer unit is configured to analyze a single reaction vessel.

[00170] Aspect 62: The system according to any preceding aspect, wherein the NIR spectrometer unit is configured to analyze a plurality of reaction vessels.

[00171] Aspect 63: The system according to any preceding aspect, wherein NIR spectrometer unit is configured to analyze the plurality of reaction vessels simultaneously or in parallel.

[00172] Aspect 64: The system according to any preceding aspect, wherein the NIR unit is configured to provide measured absorbance or spectroscopic data which are evaluated as described herein.

[00173] Aspect 65: The system according to any preceding aspect, wherein the NIR spectrometer unit is configured to irradiate each of the plurality of individual polycondensation reaction mixtures with at least one wavelength of near infrared radiation and configured to determine the absorbance spectrum of each of the plurality of individual polycondensation reaction mixtures.

[00174] Aspect 66: The system according to any preceding aspect, wherein the absorbance spectrum measured by the NIR spectrometer unit comprises at least one wavelength in the range of from 800 nm to 2500 nm.

[00175] Aspect 67: The system according to any preceding aspect, wherein the absorbance spectrum comprises at least one wavelength in the range of from 1500 nm to 2000 nm.

[00176] Aspect 68: The system according to any preceding aspect, wherein absorbance spectrum comprises multiple wavelengths.

[00177] Aspect 69: The system according to any preceding aspect, wherein absorbance spectrum comprises an entire absorption band.

[00178] Aspect 70: The system according to any preceding aspect, wherein the computing device unit is configured to receive the determined absorbance spectrum data from the NIR spectroscopic unit, and configured to perform mathematical analysis of the determined absorbance spectrum to extract chemical information.

[00179] Aspect 71: The system according to any preceding aspect, wherein the chemical information comprises the concentration of at least one reaction component.

[00180] Aspect 72: The system according to any preceding aspect, wherein mathematical analysis comprises determining the concentration of at least one reaction component using the determined absorbance spectrum.

[00181] Aspect 73: The system according to any preceding aspect, wherein the computing device unit comprises computing hardware and software for performing mathematical analysis of the determined absorbance spectrum to extract chemical information.

[00182] Aspect 74: The system according to any preceding aspect, wherein the software performs one or more steps relating to application of mathematical analysis techniques to extract chemical information.

[00183] Aspect 75: The system according to any preceding aspect, wherein one wavelength of the absorbance spectrum is used to determine a concentration of at least one reaction component.

[00184] Aspect 76: The system according to any preceding aspect, wherein determining the concentration of at least one reaction component comprises univariate analysis.

[00185] Aspect 77: The system according to any preceding aspect, wherein multiple wavelengths are used to determine the concentration of at least one reaction component.

[00186] Aspect 78: The system according to any preceding aspect, wherein determining the concentration of at least one reaction components comprises multivariate analysis.

[00187] Aspect 79: The system according to any preceding aspect, wherein multivariate analysis comprises neural networks analysis, principal components analysis, partial least squares analysis, linear multivariate analysis, or nonlinear multivariate analysis.

[00188] Aspect 80: The system according to any preceding aspect, wherein determining an intrinsic reactivity comprises comparing the degree of conversion exhibited by a polycondensation reactant with the degree of conversion of a known reference sample tested in substantially the same reaction conditions.

[00189] Aspect 81: The system according to any preceding aspect, wherein the intrinsic reactivity is used to determine deactivation kinetics of the polycondensation reaction mixture.

[00190] Aspect 82: The system according to any preceding aspect, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 30%.

[00191] Aspect 83: The system according to any preceding aspect, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 25%.

[00192] Aspect 84: The system according to any preceding aspect, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 95%.

[00193] Aspect 85: The system according to any preceding aspect, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 98%.

[00194] Aspect 86: The system according to any preceding aspect, wherein at least a portion of the system is automated.

[00195] Aspect 87: The system according to any preceding aspect, wherein at least a portion of steps are performed by a robotic device.

[00196] Aspect 88: The system according to any preceding aspect, wherein at least a portion of the system is electrically powered.

[00197] Without further elaboration, it is believed that one skilled in the art can, using the description herein, utilize the present invention. The following examples are included to provide addition guidance to those skilled in the art of practicing the claimed invention. The examples provided are merely representative of the work and contribute to the teaching of the

present invention. Accordingly, these examples are not intended to limit the invention in any manner.

[00198] While aspects of the present invention can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of skill in the art will understand that each aspect of the present invention can be described and claimed in any statutory class. Unless otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

[00199] Throughout this application, various publications are referenced. The disclosures of these publications in their entireties are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein can be different from the actual publication dates, which can require independent confirmation.

EXAMPLES

[00200] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how the compounds, compositions, articles, devices and/or methods claimed herein are made and evaluated, and are intended to be purely exemplary and are not intended to limit the disclosure. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C or is at ambient temperature, and pressure is at or near atmospheric. Unless indicated otherwise, percentages referring to composition are in terms of wt.%.

[00201] There are numerous variations and combinations of reaction conditions, e.g., component concentrations, desired solvents, solvent mixtures, temperatures, pressures and

other reaction ranges and conditions that can be used to optimize the product purity and yield obtained from the described process. Only reasonable and routine experimentation will be required to optimize such process conditions.

[00202] The materials shown in Table 1 were used to prepare the compositions described and evaluated herein.

Table 1.

Item	Description	Supplier
BPA	Bisphenol A	SABIC IP
DPC	Diphenyl carbonate	SABIC IP
KOH	Potassium hydroxide	Sigma Aldrich

[00203] In each of the examples, the samples described herein were prepared in a 250 milliliter (ml) three necked flask reactor. The flask was charged with measured amounts of DPC and BPA. Next, 0.001 N KOH (where N=normal) solution were added. After assembly, the flask was sealed and placed in an oil bath. Next, the air in the headspace was exchanged multiple times using alternating cycles of vacuum and nitrogen filling. Following the final nitrogen exchange, the bath temperature was increased to 180 °C. Once the flask achieved the target temperature, a timer was started to log reaction time. After a predetermined period, samples were taken and analyzed using the techniques and systems described herein.

[00204] High Performance Liquid Chromatography (HPLC) Analysis of the polycondensation reaction mixture samples described herein was performed using a Waters X-Terra C18 column (Waters, Milford, MA) with dimensions of 150 x 2.1 millimeters (mm) with 0.2% acetic acid (phase A) and acetonitrile (phase B) as the mobile phase. Gradient elution was as follows: 0 minutes (min) and 40% B, 3 min and 40% B, 40 min and 100% B and 45% and 100% B at a flow of 1 milliliters per minute (mL/min). The detector used was a UV-Visible diode array at a constant wavelength of 245 nm.

[00205] Near infrared spectra for each polycondensation reaction mixture sample described herein was obtained using a Bomem MB160 Near-IR Spectrometer. Spectrometer parameters were set for open beam experiment, using the spectra range of 4000-10000 inverse centimeters (cm^{-1}) and with a 4 cm^{-1} resolution.

[00206] Mathematical analysis as described herein was performed using TQ analyst quantification software. Principal component analysis was conducted for the 3 major components for each polycondensation reaction mixture sample described herein.

[00207] GRR was calculated using the equation:

$$GRR(\%) = \frac{5.15\sigma_m}{T} \times 100,$$

where σ_m is the standard deviation of a series of measurements conducted by different assays on the same sample and T is the tolerance of the measurement. When the number of samples used in the measurement is below 10, the standard deviation should be estimated by:

$$\sigma_m \approx \frac{R_{avg}}{d^*},$$

where R_{avg} is the average of the ranges in the measurements between assays and d^* is a parameter which is a function of the number of assays and the number of samples used to conduct the repeatability test.

[00208] BPA conversion was calculated using the following formula:

$$BPA \text{ conversion } (\%) = 100 \times \left(1 - \frac{\text{Final BPA concentration}}{\text{Initial BPA concentration}} \right)$$

Example 1

[00209] In Example 1, the repeatability and variability of conventional reactivity tests were investigated. To prepare the samples used in example 1, the reactor was charged with 117.7 grams (g) of DPC and 114 g of BPA. Next, 0.6 ml of 0.001 N KOH solution was added, and placed in an oil bath. After 2 hours, samples were taken and measured using HPLC analysis.

[00210] For each assay, standard amounts from identical BPA and DPC samples were added to the corresponding assays in order to confirm genuine replicates for each reactivity test. Results for the reactivity test are shown in Table 2 below.

[00211] As shown in Table 2, the conventional testing methods failed to produce an acceptable level of repeatability. Mean result for the BPA conversion measurements was 51.9 +/- 9% (95% confidence interval). The Gage Repeatability and Reproducibility (GRR) of the test, for a 40% tolerance, was 115%. Generally, most references recommend an upper limit for GRR of 30%.

Table 2*.

Sample No.	Assay A	Assay B
1	47.85	44.30
2	43.92	26.87
3	62.19	55.84

Sample No.	Assay A	Assay B
4	38.01	62.65
5	73.50	64.53

* Amounts provided in terms of percent of total composition (by weight).

Example 2

[00212] Example 2 illustrates the estimated influence of the number of replicates on test variability. A self-developed, first principles model for the simulation of the reaction system was designed using MATLAB as a software platform. Next, random noise was injected into the model in order to simulate the fit the lack of repeatability observed in the experimental results obtained in Example 1. Using this simulation software, several simulated runs were executed in order to investigate the influence of the number of replicates in the reduction of the test variability. Results of simulations for N = 6, N= 24 and N = 96 are shown in FIG. 1 and a correlation of test standard deviation as a function of the number of replicates is pictured in FIG. 2. As seen in FIG. 2, predicted reduction of confidence interval moves from 10.7% for N = 6 to 1.8% for N = 96.

Example 3

[00213] Using the preparation methods described herein, synthetic mixtures of BPA, DPC, phenol and oligomers were prepared. The mixtures comprised a BPA composition ranging from 0 to 30% in terms of percent of the total mixture (by weight). HPLC analysis was then carried out on a sample from each mixture to determine a precise chemical composition. Next, a sample from each mixture was analyzed using NIR spectroscopy methods described herein. 0.25 g of each sample was dissolved in 25 ml of dichloromethane and placed in a 10 mm infrared cuvette. Next, the measured near-infrared spectra data was processed as described herein for principal component analysis of 3 major components (phenol, BPA and DPC). Following calibration, the data produced a perfect correlation between HPLC composition of each component and their absorbance (regression coefficient = 1.000 for all components). NIR spectrum and correlation plot for BPA is displayed in FIG. 3.

Example 4

[00214] Using the preparation methods described herein, synthetic mixtures of BPA, DPC, phenol and oligomers were prepared. The mixtures comprised a BPA composition ranging from 0 to 30% in terms of percent of the total mixture (by weight). HPLC analysis as

described herein was then carried out on a sample from each mixture to determine the precise chemical composition. Next, a corresponding sample from each mixture was analyzed using NIR spectroscopy methods described herein. Here, the samples for NIR analysis were heated to 80 °C and measured directly with no solvent intervention. Next, the measured near-infrared spectra data was processed as described herein for principal component analysis of 3 major components (phenol, BPA and DPC). Following calibration, the data again produced a very good correlation between HPLC composition of each component and their absorbance (regression coefficients = 0.9804, 0.9824, 0.9761 for phenol, BPA and DPC, respectively). NIR spectrum and correlation plot for BPA is displayed in FIG. 4.

[00215] The patentable scope of the invention is defined by the claims, and can include other examples that occur to those skilled in the art. Such other examples are intended to be within the scope of the claims if they have structural elements that do not differ from the literal language of the claims, or if they include equivalent structural elements with insubstantial differences from the literal languages of the claims.

CLAIMS

What is claimed is:

1. A method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising:
 - (a) providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants;
 - (b) simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product;
 - (c) analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures;
 - (d) determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and
 - (e) determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures.
2. The method of claim 1, wherein the polycondensation reaction mixture comprises a polycarbonate polymerization reaction mixture.
3. The method of any preceding claim, wherein the reaction component comprises starting reactants, chemical intermediates, reaction by-products, or end products, or combinations thereof.
4. The method according to any preceding claim, wherein the reaction component comprises bisphenol A, diphenyl carbonate, an oligomer, phenol, or a polycarbonate polymer, or combinations thereof.
5. The method according to any preceding claim, wherein the reaction component is present in an amount from greater than 0 weight% to 100 weight % of polycondensation reaction mixture.

6. The method according to any preceding claim, wherein the reaction component comprises DPC.
7. The method according to any preceding claim, wherein the reaction component comprises BPA.
8. The method according to any preceding claim, wherein the reaction component comprises phenol.
9. The method according to any preceding claim, wherein the polycondensation reactants comprise an aromatic dihydroxy compound or a diaryl carbonate ester.
10. The method according to any preceding claim, wherein the polycondensation reactants comprise bisphenol A (BPA) or diphenyl carbonate (DPC).
11. The method according to any preceding claim, wherein conditions effective comprise reaction conditions of a melt polymerization reaction.
12. The method according to any preceding claim, wherein the plurality of reaction mixtures comprises an array.
13. The method according to any preceding claim, wherein the plurality of reaction mixtures comprises a first-order array.
14. The method according to any preceding claim, wherein the plurality of reaction mixtures comprises a second-order or higher array.
15. The method according to any preceding claim, wherein the plurality of reaction mixtures comprises a multi-order array.
16. The method according to any preceding claim, wherein the plurality of reaction mixtures comprise a multi-well microtiter plate.
17. The method according to any preceding claim, wherein the plurality of reaction mixtures comprise individual samples, multiple individual samples arranged in a fixed configuration, or a plurality of individual samples.
18. The method according to any preceding claim, wherein analyzing each of the plurality of individual polycondensation reaction mixtures is substantially simultaneous.
19. The method according to any preceding claim, wherein analyzing each of the plurality of individual polycondensation reaction mixtures is separate.
20. The method according to any preceding claim, further comprising simultaneously subjecting the plurality of the second polycondensation reaction mixtures to conditions effective to terminate the reaction.

21. The method according to any preceding claim, wherein the polycondensation product comprises a polycarbonate product or intermediate polycarbonate product.

22. The method according to any preceding claim, wherein analyzing comprises irradiating each of the plurality of individual polycondensation reaction mixtures with at least one wavelength of near infrared radiation and measuring the absorbance spectrum of each of the plurality of individual polycondensation reaction mixtures, and correlating absorbance values to levels of a reaction component.

23. The method according to any preceding claim, wherein absorbance spectrum comprises at least one wavelength in the range of from 800 nm to 2500 nm.

24. The method according to any preceding claim, wherein absorbance spectrum comprises at least one wavelength in the range of from 1500 nm to 2000 nm.

25. The method according to any preceding claim, wherein absorbance spectrum comprises multiple wavelengths.

26. The method according to any preceding claim, wherein absorbance spectrum comprises an entire absorption band.

27. The method according to any preceding claim, wherein one wavelength is used to determine a concentration of one or more reaction components.

28. The method according to any preceding claim, wherein determining a concentration of one or more reaction components comprises univariate analysis.

29. The method according to any preceding claim, wherein multiple wavelengths are used to determine a concentration of one or more reaction components.

30. The method according to any preceding claim, wherein determining a concentration of one or more reaction components comprises multivariate analysis.

31. The method according to any preceding claim, wherein multivariate analysis comprises neural networks analysis, principal components analysis, partial least squares analysis, linear multivariate analysis, or nonlinear multivariate analysis.

32. The method according to any preceding claim, wherein at least one step in determining a concentration of one or more reaction components is performed using computer software.

33. The method according to any preceding claim, wherein determining an intrinsic reactivity comprises comparing the degree of conversion exhibited by a polycondensation reactant with the degree of conversion of a known reference sample tested in substantially the same reaction conditions.

34. The method according to any preceding claim, wherein the intrinsic reactivity is used to determine deactivation kinetics of the polycondensation reaction mixture.

35. The method according to any preceding claim, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 30%.

36. The method according to any preceding claim, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 25%.

37. The method according to any preceding claim, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 95%.

38. The method according to any preceding claim, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 98%.

39. A method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising:

- (a) providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants;
- (b) simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product;
- (c) simultaneously subjecting the plurality of the second polycondensation reaction mixtures to conditions effective to terminate the reaction;
- (d) analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures;
- (e) determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and
- (f) determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures.

40. A method for determining an intrinsic reactivity value of a polycondensation reaction mixture, the method comprising:

- (a) providing a plurality of at least substantially identical first polycondensation reaction mixtures from a single batch of polycondensation reactants comprising bisphenol A (BPA) and diphenyl carbonate (DPC);
- (b) simultaneously subjecting the plurality of at least substantially identical first polycondensation reaction mixtures to conditions effective to result in a formation of a plurality of second polycondensation reaction mixtures, each comprising at least one polycondensation product;
- (c) analyzing each of the plurality of second polycondensation reaction mixtures using near infrared spectroscopy to determine an absorbance spectrum of each of the plurality of second polycondensation reaction mixtures;
- (d) determining a concentration of one or more components present in each of the plurality of second polycondensation reaction mixtures from each absorbance spectrum; and
- (e) determining an intrinsic reactivity value of the single batch of polycondensation reactants from the determined concentration of the one or more components present in each of the plurality of second polycondensation reaction mixtures;
wherein the components comprise BPA, DPC, phenol, or combinations thereof.

41. A system for determining an intrinsic reactivity value of a polycondensation reaction mixture, the system comprising:

- (a) a reaction unit comprising a plurality of reaction vessels;
- (b) at least one dispensing unit for dispensing a single batch of polycondensation reactants into each of the plurality of reaction vessels such that each reaction vessel contains a substantially identical first polycondensation reaction mixture;
- (c) a means for simultaneously subjecting each of the first polycondensation reaction mixtures to conditions effective to result in each first polycondensation reaction mixture forming a second polycondensation reaction mixture comprising a polycondensation product;

- (d) a means for simultaneously subjecting each of the second polycondensation reaction mixtures to conditions effective to result in termination of the reaction;
- (e) a near infrared spectrometer unit configured to analyze each second polycondensation reaction mixture and to determine an absorbance spectrum of each second polycondensation reaction mixture; and
- (f) a computing device unit configured to determine an intrinsic reactivity value of the single batch of polycondensation reactants from the determined absorbance spectrum of each second polycondensation reaction mixture.

42. The system of claim 41, wherein the reaction unit comprises individual reaction vessels, multiple individual vessels arranged in a fixed configuration, or a plurality of individual vessels.

43. The system according to any preceding claim, wherein the reaction unit comprises an array.

44. The system according to any preceding claim, wherein the reaction unit comprises a first-order array, a second-order array, or a multi-order array, or combinations thereof.

45. The system according to any preceding claim, wherein the reaction unit comprises a multi-well microtiter plate.

46. The system of claim 45, wherein the multi-well microtiter plate comprises a 96-well, 192-well, or 384-well microtiter plate.

47. The system according to any preceding claim, wherein the reaction vessels comprise glass or quartz vials.

48. The system according to any preceding claim, wherein the dispensing unit comprises a gravimetric dispensing system or a volumetric dispensing system.

49. The system according to any preceding claim, wherein the polycondensation reactants are dispensed in the reaction vessels simultaneously or successively.

50. The system according to any preceding claim, wherein the means for simultaneously subjecting to conditions effective comprises an admixing unit.

51. The system according to any preceding claim, wherein the admixing unit shakes or agitates the reaction unit or reaction vessels to cause mixing of the polycondensation reactants.

52. The system according to any preceding claim, wherein the admixing unit comprises a means for stirring the plurality of polycondensation reaction mixtures.

53. The system according to any preceding claim, wherein the means for stirring comprises a plurality of stirring instruments.

54. The system according to any preceding claim, wherein each of the plurality of stirring instruments corresponds to a reaction vessel.

55. The system according to any preceding claim, wherein the means for simultaneously subjecting conditions effective comprise a temperature control unit.

56. The system according to any preceding claim, wherein the temperature control unit comprises a heating unit, or a cooling unit, or a combination thereof.

57. The system according to any preceding claim, wherein the heating unit comprises a heating element.

58. The system according to any preceding claim, wherein the heating element comprises a heat plate, heat lamp, or heating bath.

59. The system according to any preceding claim, the cooling unit comprises a cooling element.

60. The system according to any preceding claim, wherein the cooling element comprises a refrigerated bath.

61. The system according to any preceding claim, wherein the near infrared spectrometer unit is configured to analyze a single reaction vessel.

62. The system according to any preceding claim, wherein the NIR spectrometer unit is configured to analyze a plurality of reaction vessels.

63. The system according to any preceding claim, wherein NIR spectrometer unit is configured to analyze the plurality of reaction vessels simultaneously or in parallel.

64. The system according to any preceding claim, wherein the NIR unit is configured to provide measured absorbance or spectroscopic data which are evaluated as described herein.

65. The system according to any preceding claim, wherein the NIR spectrometer unit is configured to irradiate each of the plurality of individual polycondensation reaction mixtures with at least one wavelength of near infrared radiation and configured to determine the absorbance spectrum of each of the plurality of individual polycondensation reaction mixtures.

66. The system according to any preceding claim, wherein the absorbance spectrum measured by the NIR spectrometer unit comprises at least one wavelength in the range of from 800 nm to 2500 nm.

67. The system according to any preceding claim, wherein the absorbance spectrum comprises at least one wavelength in the range of from 1500 nm to 2000 nm.

68. The system according to any preceding claim, wherein absorbance spectrum comprises multiple wavelengths.

69. The system according to any preceding claim, wherein absorbance spectrum comprises an entire absorption band.

70. The system according to any preceding claim, wherein the computing device unit is configured to receive the determined absorbance spectrum data from the NIR spectroscopic unit, and configured to perform mathematical analysis of the determined absorbance spectrum to extract chemical information.

71. The system according to any preceding claim, wherein the chemical information comprises the concentration of at least one reaction component.

72. The system according to any preceding claim, wherein mathematical analysis comprises determining the concentration of at least one reaction component using the determined absorbance spectrum.

73. The system according to any preceding claim, wherein the computing device unit comprises computing hardware and software for performing mathematical analysis of the determined absorbance spectrum to extract chemical information.

74. The system according to any preceding claim, wherein the software performs one or more steps relating to application of mathematical analysis techniques to extract chemical information.

75. The system according to any preceding claim, wherein one wavelength of the absorbance spectrum is used to determine a concentration of at least one reaction component.

76. The system according to any preceding claim, wherein determining the concentration of at least one reaction component comprises univariate analysis.

77. The system according to any preceding claim, wherein multiple wavelengths are used to determine the concentration of at least one reaction component.

78. The system according to any preceding claim, wherein determining the concentration of at least one reaction components comprises multivariate analysis.

79. The system according to any preceding claim, wherein multivariate analysis comprises neural networks analysis, principal components analysis, partial least squares analysis, linear multivariate analysis, or nonlinear multivariate analysis.

80. The system according to any preceding claim, wherein determining an intrinsic reactivity comprises comparing the degree of conversion exhibited by a polycondensation reactant with the degree of conversion of a known reference sample tested in substantially the same reaction conditions.

81. The system according to any preceding claim, wherein the intrinsic reactivity is used to determine deactivation kinetics of the polycondensation reaction mixture.

82. The system according to any preceding claim, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 30%.

83. The system according to any preceding claim, wherein the Gage repeatability and reproducibility (GRR) is less than or equal to 25%.

84. The system according to any preceding claim, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 95%.

85. The system according to any preceding claim, wherein the number of polycondensation reaction mixtures analyzed is sufficient to produce a predicted confidence interval of at least about 98%.

86. The system according to any preceding claim, wherein at least a portion of the system is automated.

87. The system according to any preceding claim, wherein at least a portion of steps are performed by a robotic device.

88. The system according to any preceding claim, wherein at least a portion of the system is electrically powered.

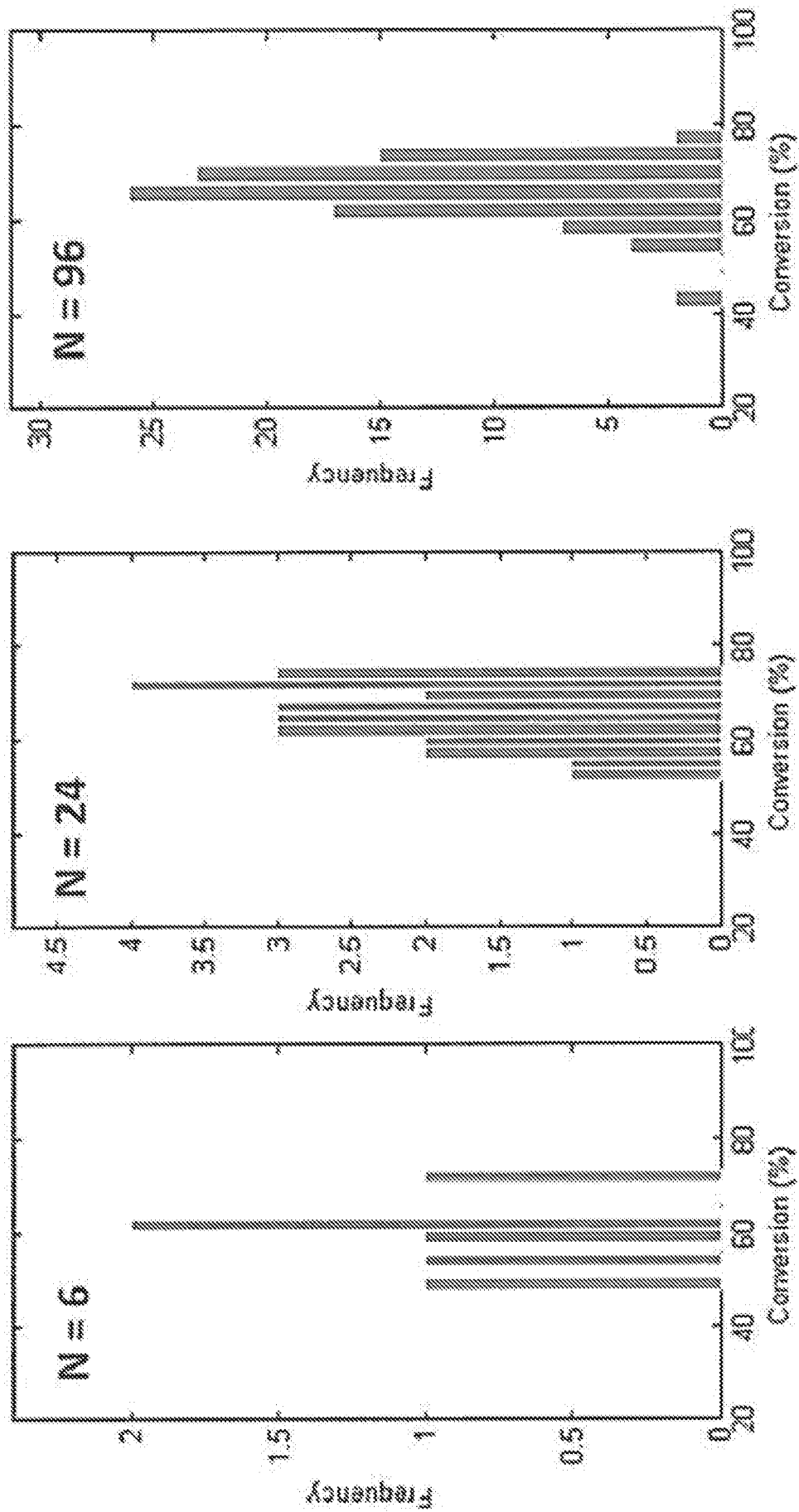


FIG. 1

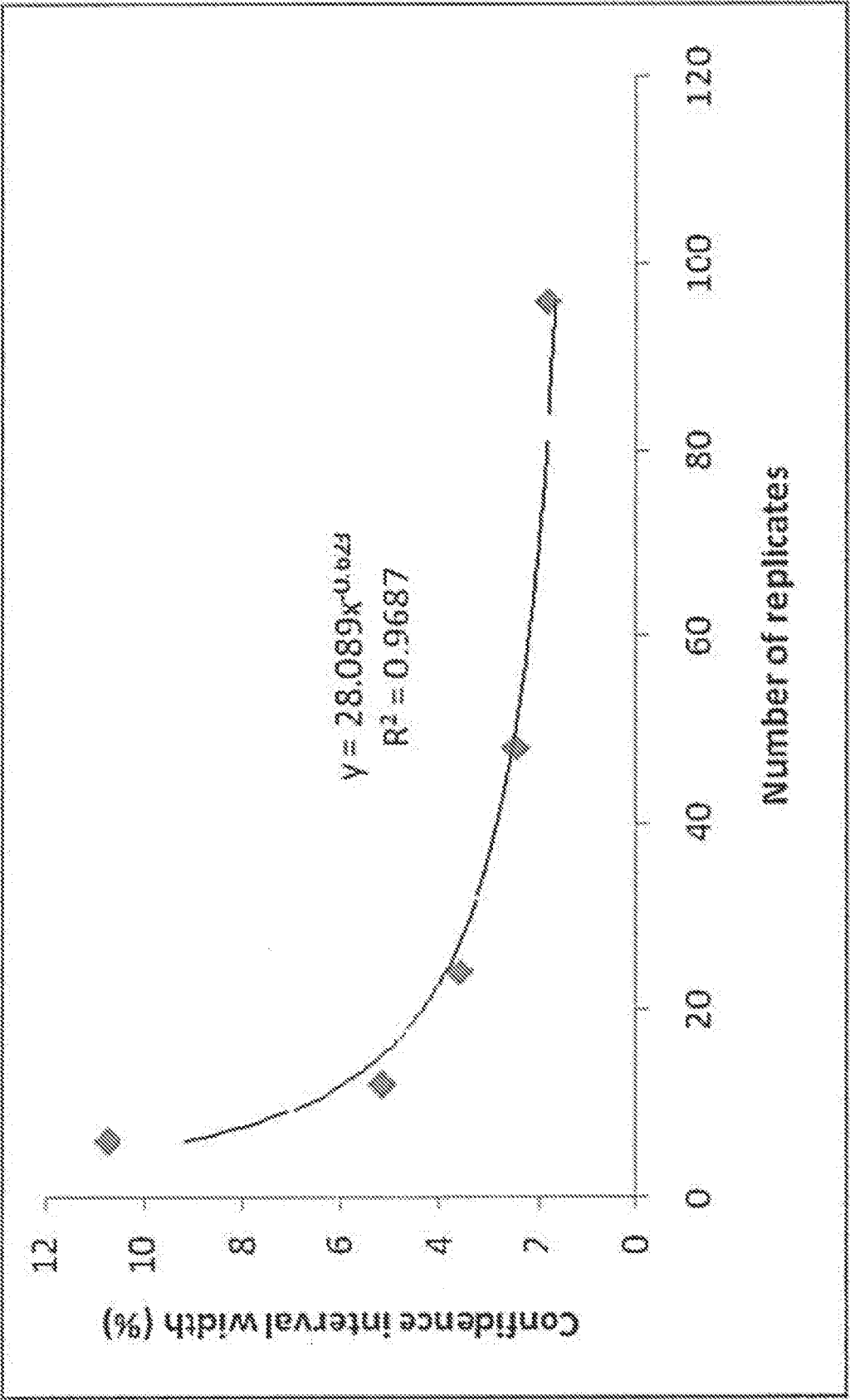


FIG. 2

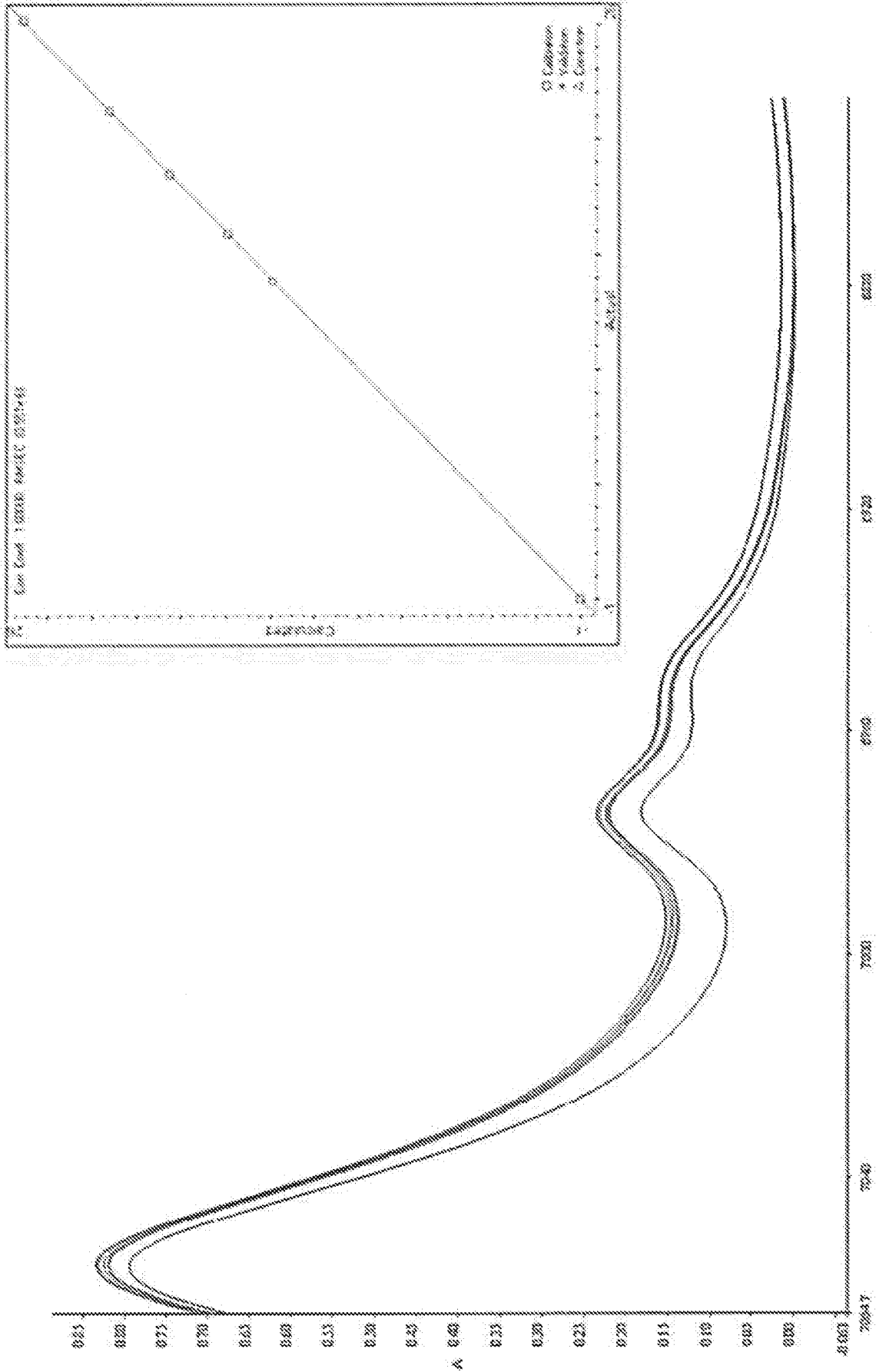


FIG. 3

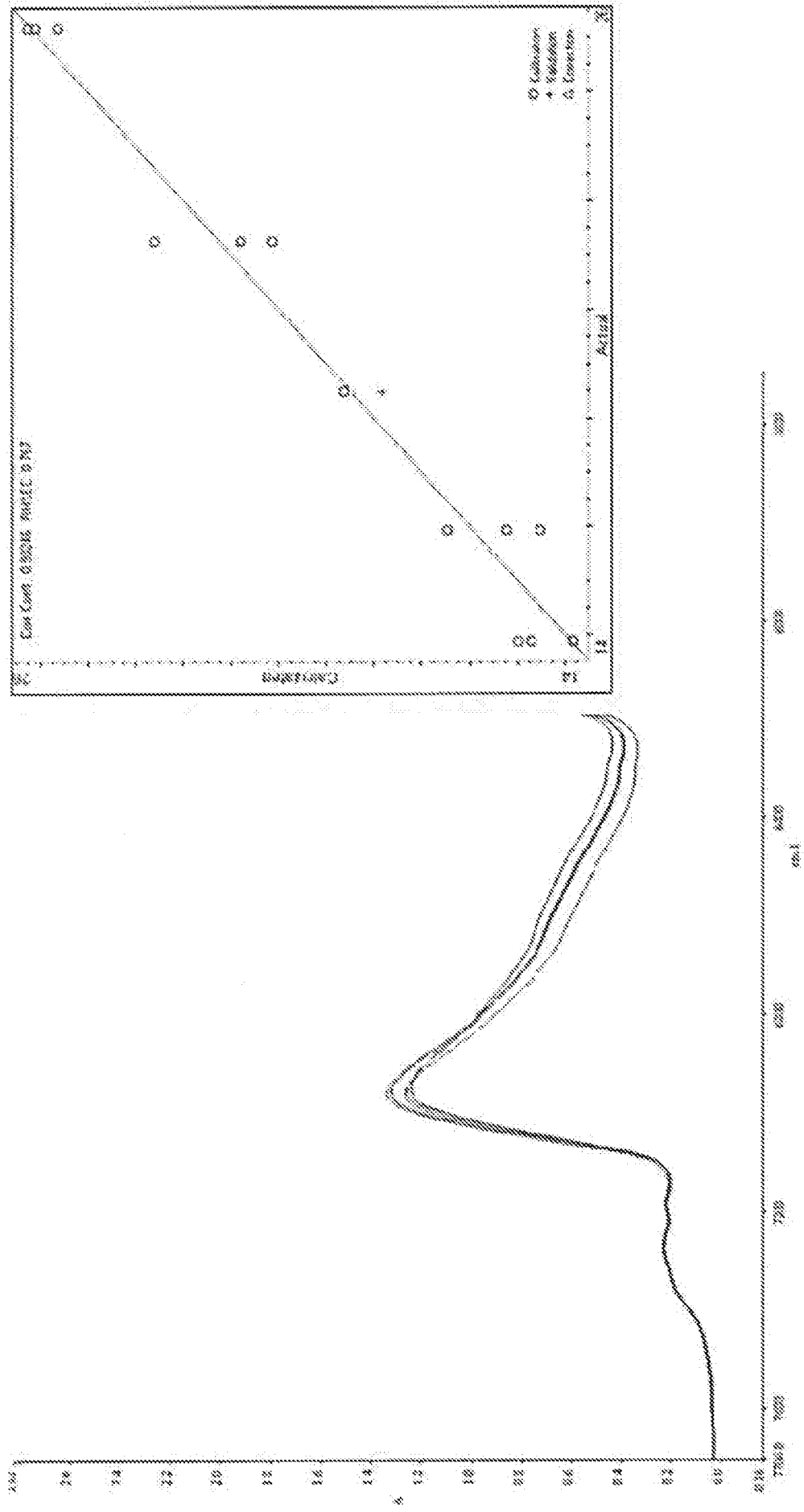


FIG. 4

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2014/061599

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G64/20
ADD.

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)
C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2005 017893 A1 (BAYER MATERIALSCIENCE AG [DE]) 26 October 2006 (2006-10-26) example 1	1-88
X	----- EP 0 926 181 A2 (GEN ELECTRIC [US] GEN ELECTRIC) 30 June 1999 (1999-06-30) paragraph [0171] -----	1-88



Further documents are listed in the continuation of Box C.



See patent family annex.

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"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

Date of the actual completion of the international search

2 September 2014

Date of mailing of the international search report

09/09/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2014/061599

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102005017893 A1	26-10-2006	NONE	
EP 0926181 A2	30-06-1999	CN 1225926 A	18-08-1999
		DE 69822424 D1	22-04-2004
		DE 69822424 T2	17-02-2005
		EP 0926181 A2	30-06-1999
		JP 3681529 B2	10-08-2005
		JP H11189643 A	13-07-1999
		TW 523527 B	11-03-2003
		US 2002037838 A1	28-03-2002