

POLYPHENYLENE OLIGOMERS AND POLYMERS

This invention relates to polyphenylene oligomers and polymers and processes for preparing and using the same. Such oligomers and polymers may be useful
5 as dielectric resins in microelectronics fabrication.

This Application is a continuation-in-part of Application Serial No. 711,838; filed September 10, 1996, which is incorporated herein by reference.

Polymer dielectrics may be used as insulating layers between various circuits and layers within circuits in microelectronic devices such as integrated circuits, multichip
10 modules, and laminated circuit boards. The microelectronics fabrication industry is moving toward smaller geometries in its devices to enable lower power and faster speeds. As the conductor lines become finer and more closely packed, the requirements of the dielectrics between such conductors become more stringent.

While polymer dielectrics often provide lower dielectric constants than
15 inorganic dielectrics such as silicon dioxide, they often present challenges to process integration during fabrication. For example, to replace silicon dioxide as a dielectric in integrated circuits, the dielectric must be able to withstand processing temperatures during metallization and annealing steps of the process. Preferably, the dielectric material should have a glass transition temperature greater than the processing temperature. The dielectric
20 must also retain the desirable properties under device use conditions. For example, the dielectric should not absorb water which may cause an increase in the dielectric constant and potential corrosion of metal conductors.

For some integration schemes, the oligomer should preferably planarize and gap fill a patterned surface when applied by conventional application techniques such as spin
25 coating.

Currently, polyimide resins are one class of materials which are employed as thin film dielectrics in the electronics industry. However, polyimide resins may absorb water and hydrolyze which can lead to circuit corrosion. Metal ions may migrate into the dielectric polyimide layer requiring a barrier layer between the metal lines and polyimide dielectric.
30 Polyimides may exhibit poor planarization and gap fill properties. Non-fluorinated polyimides may exhibit undesirably high dielectric constants.

Kumar and Neenan, in Macromolecules, 1995, 28, pp 124-130, disclose numerous polyphenylenes made from biscyclopentadienones and bisacetylenes. They teach that the polyphenylenes have potential as photodefineable organic dielectrics. Wrasidlo and
35 Augl, in J. Polym. Sci., Part B (1969), 7(7), 519-523, disclose the copolymerization of

1,4-bis(phenylethynyl)benzene with 3,3'-(1,4-phenylene)-bis(2,4,5-triphenylpentadienone).

They report a soluble, yellow, infusible polymer was obtained.

The materials described in Kumar and Wrasidlo are soluble but may not be suitable for some uses such as spin coating to fill gaps because the materials were polymerized to exhaustion of the cyclopentadienone moieties which provides relatively high molecular weights. The molecular weight may be too high to permit application by spin coating over a patterned surface containing gaps to be filled by the dielectric. Based on the reported glass transition temperatures, such materials may not be able to withstand the processing desired for interlayer dielectrics in integrated circuits.

In U. S. Patents 5,334,668; 5,236,686; 5,169,929; and 5,338,823, Tour describes several methods of preparing cross-linkable polyphenylene compositions for the preparation of glassy carbon. The polyphenylenes are made by polymerizing 1-bromo-4-lithiobenzene to form a brominated polyphenylene and then coupling substituted phenylacetylenes, such as phenylacetylenyl phenyl acetylene, to the residual bromines. The polyphenylenes have melting points around 200°C prior to crosslinking.

It would be desirable to provide a polymer dielectric to the microelectronics fabrication industry which provides a reliably low dielectric constant, high thermal stability and a high glass transition temperature and which preferably, permits application by spin coating to planarize and fill gaps on a patterned surface.

In a first aspect, the present invention is an oligomer, uncured polymer or cured polymer comprising the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups wherein at least some of the polyfunctional compounds contain three or more reactive groups.

A reactive group, as used herein, is defined as a cyclopentadienone or acetylene group. An oligomer, as used herein, is defined as a reaction product of two or more monomer units of the invention which will gap fill, that is, fill a rectangular trench which is one micrometer deep and one half micrometer across without leaving a void when cured. An uncured polymer, as used herein, is defined as a reaction product of monomers of the invention which no longer gap fills but which contains significant unreacted cyclopentadienone or acetylene functionality. A cured polymer, as used herein, is defined as a reaction product of monomers of the invention which contains no significant unreacted cyclopentadienone or acetylene functionality. Significant unreacted cyclopentadienone or acetylene functionality requires that said moieties be reactive to further advance the polymerization.

A feature of the invention is that it comprises the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups wherein at least some of the polyfunctional compounds contain three or more reactive groups. An advantage of such a reaction product is that it may gap fill and planarize patterned surfaces, and as cured have high thermal stability, a high glass transition temperature and a low dielectric constant.

In a second, preferred aspect, the present invention is an oligomer, uncured polymer or cured polymer comprising the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and one or more polyfunctional compounds containing two or more aromatic acetylene groups, wherein at least some of the polyfunctional compounds containing aromatic acetylene groups contain three or more acetylene groups.

A feature of the second aspect of the invention is that it comprises the reaction product of at least one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups, wherein at least some of the polyfunctional compounds containing aromatic acetylene groups contain three or more acetylene groups. An advantage of such a reaction product is that it may gap fill and planarize patterned surfaces, and as cured have high thermal stability, a high glass transition temperature and a low dielectric constant.

High thermal stability, a high glass transition temperature, a low dielectric constant and the ability to gap fill and planarize patterned surfaces make the compositions of the invention suitable as polymer dielectrics in microelectronics fabrication. In particular, the combination of low dielectric constant, high thermal stability and high glass transition temperature permit the use of the compositions of the invention as interlayer dielectrics in integrated circuits.

Preferably, the oligomers and polymers and corresponding starting monomers of the present invention are:

I. Oligomers and polymers of the general formula:

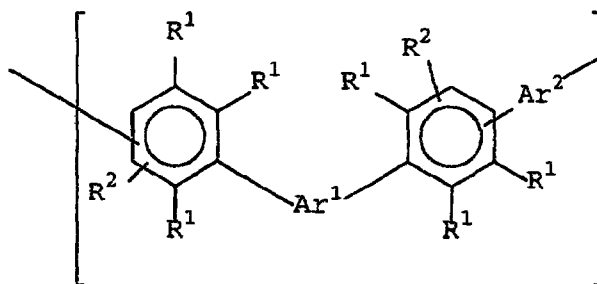


wherein A has the structure:

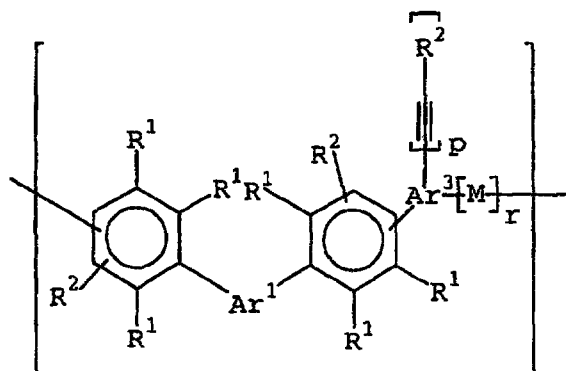
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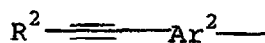
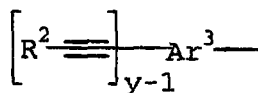
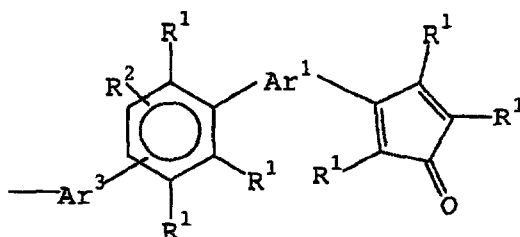
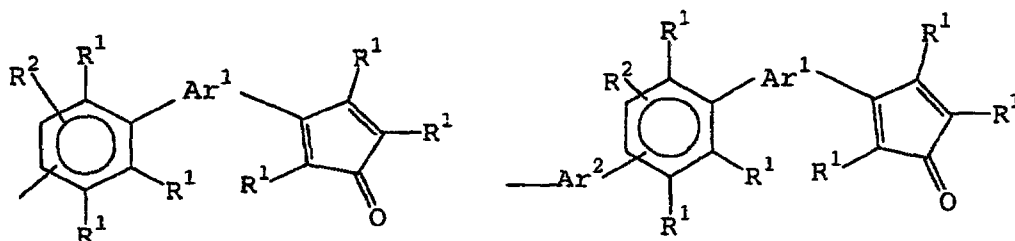


and B has the structure:



wherein EG are end groups having one or more of the structures:

EG=



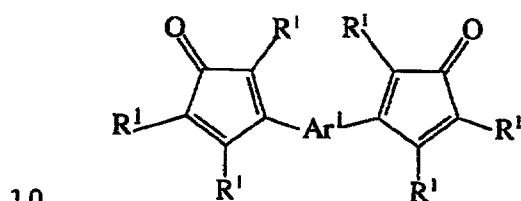
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wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹, Ar² and Ar³ are independently an unsubstituted aromatic moiety or inertly-

substituted aromatic moiety, M is a bond, and y is an integer of three or more, p is the number of unreacted acetylene groups in the given mer unit, r is one less than the number of reacted acetylene groups in the given mer unit and $p+r=y-1$, z is an integer from 0 to 1000; w is an integer from 0 to 1000 and v is an integer of two or more.

- 5 Such oligomers and polymers can be prepared by reacting a biscyclopentadienone, an aromatic acetylene containing three or more acetylene moieties and, optionally, a polyfunctional compound containing two aromatic acetylene moieties. Such a reaction may be represented by the reaction of compounds of the formulas

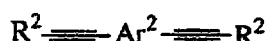
(a) a biscyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:



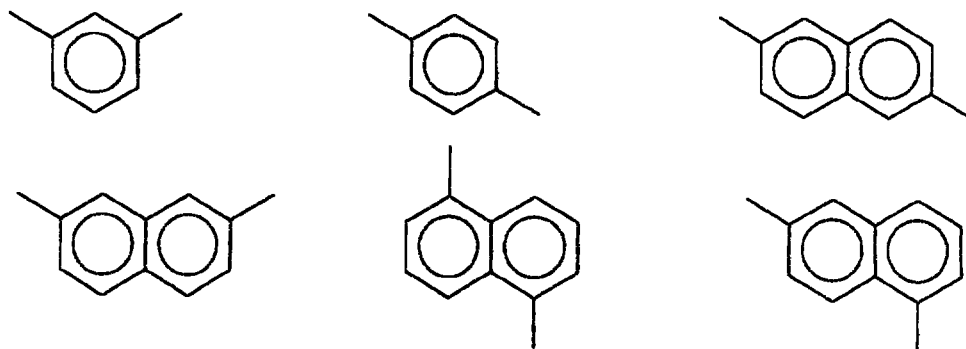
(c) and, optionally, a diacetylene of the formula:



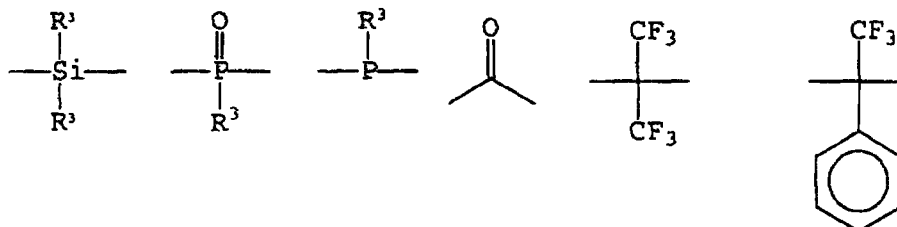
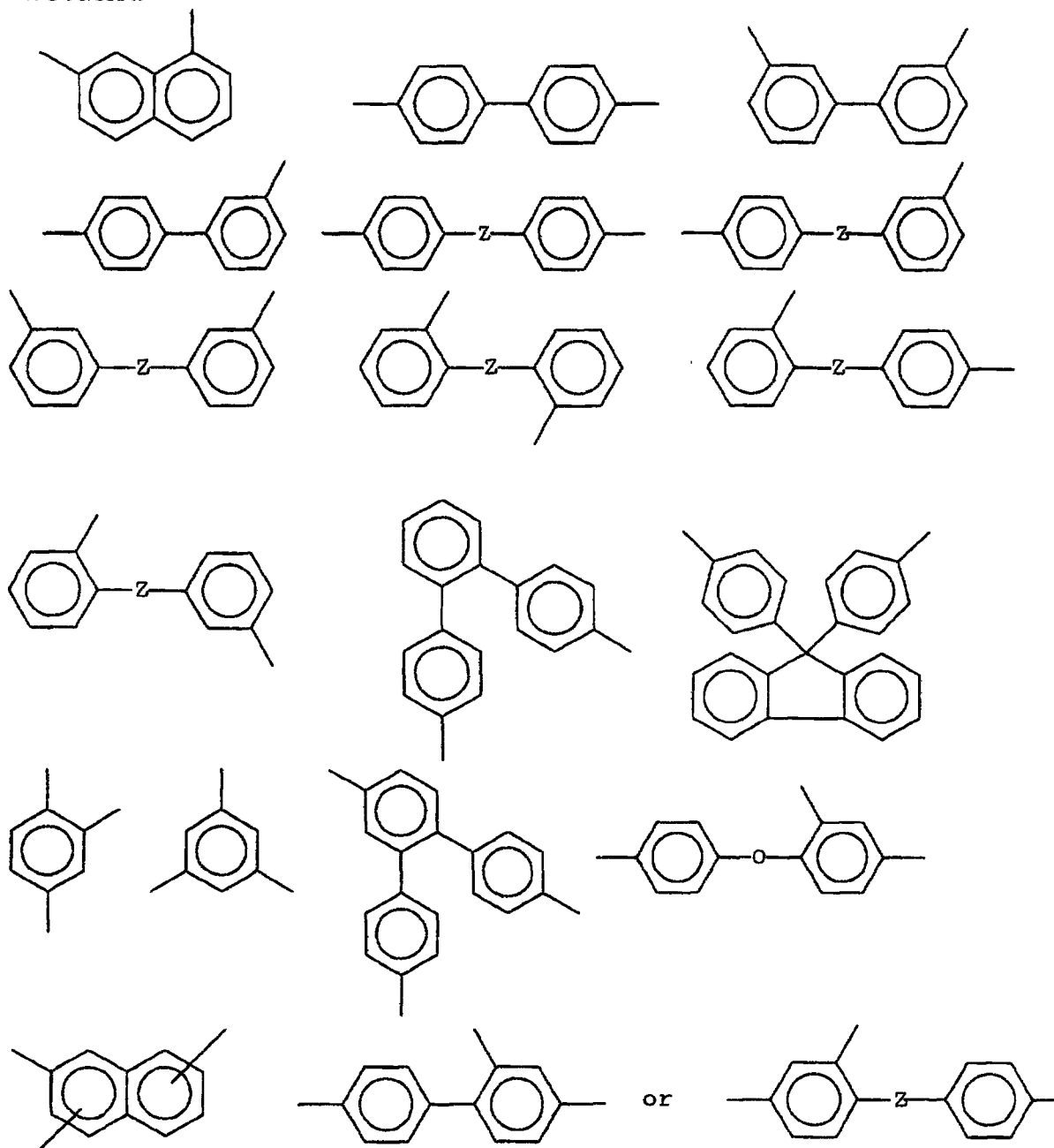
- 15 wherein R^1 , R^2 , Ar^1 , Ar^2 , Ar^3 and y are as previously defined.

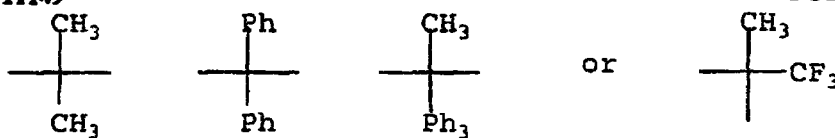
The definition of aromatic moiety includes phenyl, polyaromatic and fused aromatic moieties. Inertly-substituted means the substituent groups are essentially inert to the cyclopentadienone and acetylene polymerization reactions and do not readily react under the conditions of use of the cured polymer in microelectronic devices with environmental species such as water. Such substituent groups include, for example, F, Cl, Br, $-CF_3$, $-OCH_3$, $-OCF_3$, $-O-Ph$ and alkyl of from one to eight carbon atoms, cycloalkyl of from three to eight carbon atoms. For example, the moieties which can be unsubstituted or inertly-substituted aromatic moieties include:

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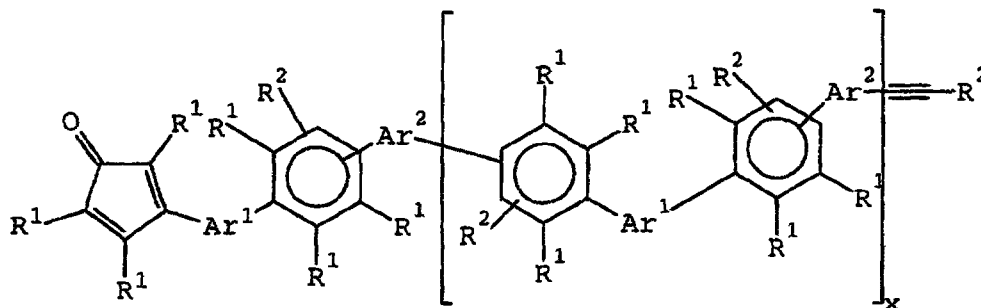
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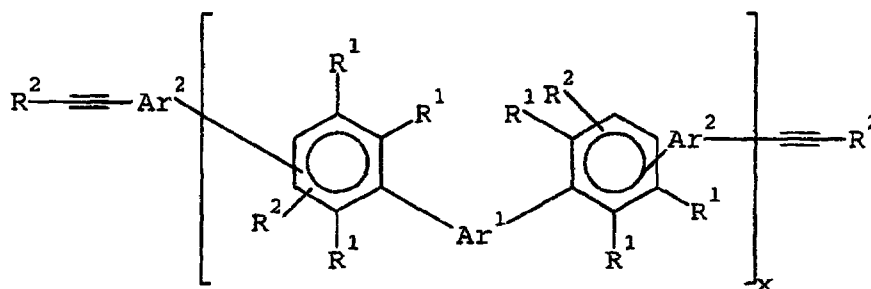
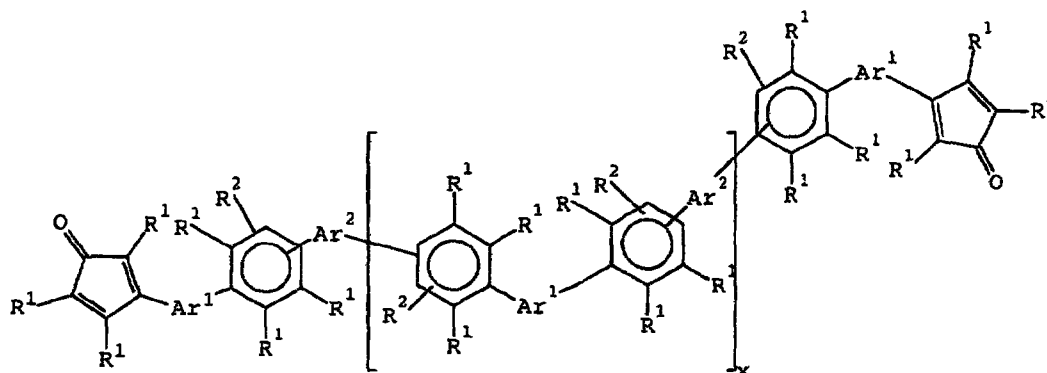


wherein each R^3 is independently -H, $-\text{CH}_3$, $-\text{CH}_2\text{CH}_3$, $-(\text{CH}_2)_2\text{CH}_3$ or Ph. Ph is phenyl.

II. Polyphenylene oligomers and polymers of the general formulas:



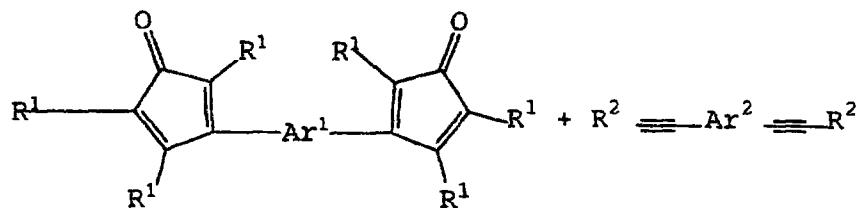
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wherein R^1 , R^2 , Ar^1 and Ar^2 are as defined previously; and x is an integer from 1 to 1000.

Preferably, x is from 1 to 50 and more preferably from 1 to ten. Such oligomers and

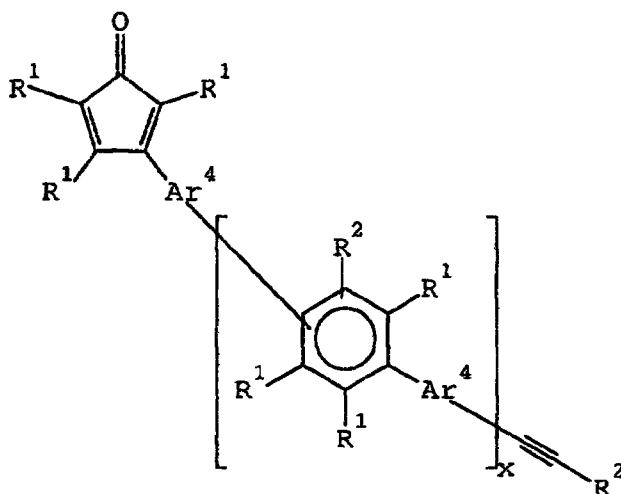
10 polymers can be prepared by the reaction of a biscyclopentadienone and a diacetylene of the



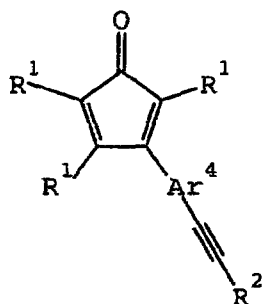
general formulas:

wherein R^1 , R^2 , Ar^1 and Ar^2 are as previously defined.

III. Polyphenylene oligomers and polymers represented by the formula:

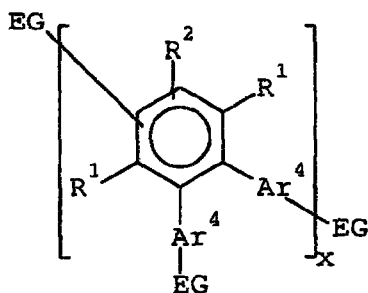


5 wherein Ar^4 is an aromatic moiety or an inertly-substituted aromatic moiety, R^1 , R^2 , and x are as previously defined, as can be prepared by the reaction of the cyclopentenone functionality and the acetylene functionality of a polyfunctional compound of the general formula:

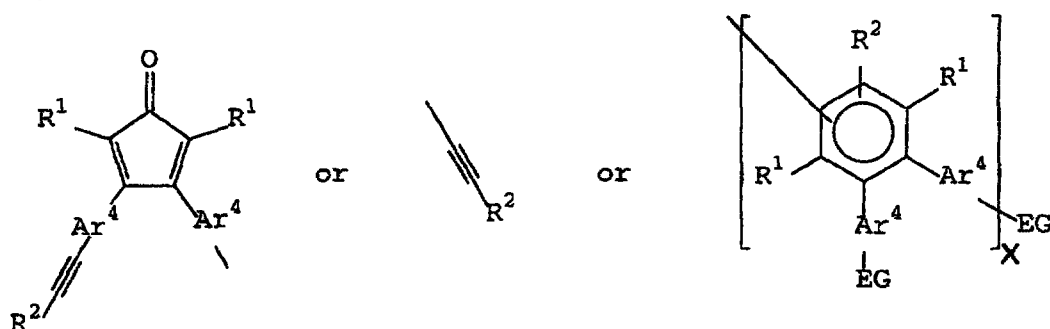


wherein R^1 , R^2 and Ar^4 are as defined previously.

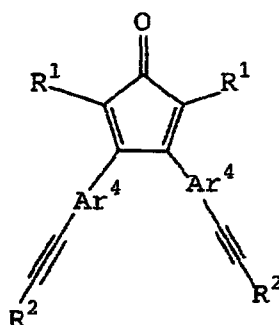
10 IV. Polyphenylene oligomers and polymers represented by the formula:



wherein EG is represented by any one of the formulas:



wherein R^1 , R^2 , Ar^4 and x are as defined previously, as can be prepared by the reaction of the cyclopentadienone functionality and the acetylene functionality of a polyfunctional compound of the general formula:



5

wherein R^1 , R^2 , and Ar^4 are as defined previously.

A polyfunctional compound containing two or more aromatic cyclopentadienone moieties may be made by the condensation of benzils with benzyl ketones using conventional methods.

Exemplary methods are disclosed in Kumar et al. *Macromolecules*, 1995, **28**, 124-130;

10 Ogliaruso et al., *J. Org. Chem.*, 1965, **30**, 3354; Ogliaruso et al., *J. Org. Chem.*, 1963, **28**, 2725; and U.S. Patent 4,400,540.

A polyfunctional compound containing two or more aromatic acetylene moieties may be made by conventional methods. An aromatic compound may be halogenated and then reacted with the appropriate substituted acetylene in the presence of an aryl ethynylation catalyst to replace the halogen with the substituted acetylene compound.

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Once the polyfunctional compound monomers are made, they are preferably purified. In particular, in preparation for use as an organic polymer dielectric, metals and ionic species are removed. For example, the polyfunctional compounds containing aromatic acetylene groups may be contacted with a water wash, an aliphatic hydrocarbon solvent and then dissolved in an aromatic solvent and filtered through a purified silica gel. This treatment can remove residual ethynylation catalyst. Additional recrystallizations may also help in removal of undesired impurities.

20

While not intended to be bound by theory, it is believed that the polyphenylene oligomers and polymers are formed through the Diels Alder reaction of the cyclopentadienone groups with the acetylene groups when the mixtures of cyclopentadienones and acetylenes in solution are heated. These oligomers may contain cyclopentadienone and/or acetylene end groups and/or pendant groups. Upon further heating of the solution or an article coated with the solution, additional chain extension can occur through the Diels Alder reaction of the remaining cyclopentadienone end groups with the remaining acetylene groups resulting in an increase in molecular weight. Depending on the temperature used, reaction of the acetylene groups with each other may also occur.

The oligomers and polymers are shown in the structures as having either cyclopentadienone and/or acetylene end groups and/or pendant groups. In general, the end groups will depend on the relative concentration of cyclopentadienone to Diels Alder reactive acetylene functionality employed in the reaction, with a stoichiometric excess of cyclopentadienone functionality giving more cyclopentadienone end groups and a stoichiometric excess of Diels Alder reactive acetylene functionality giving a greater proportion of acetylene end groups.

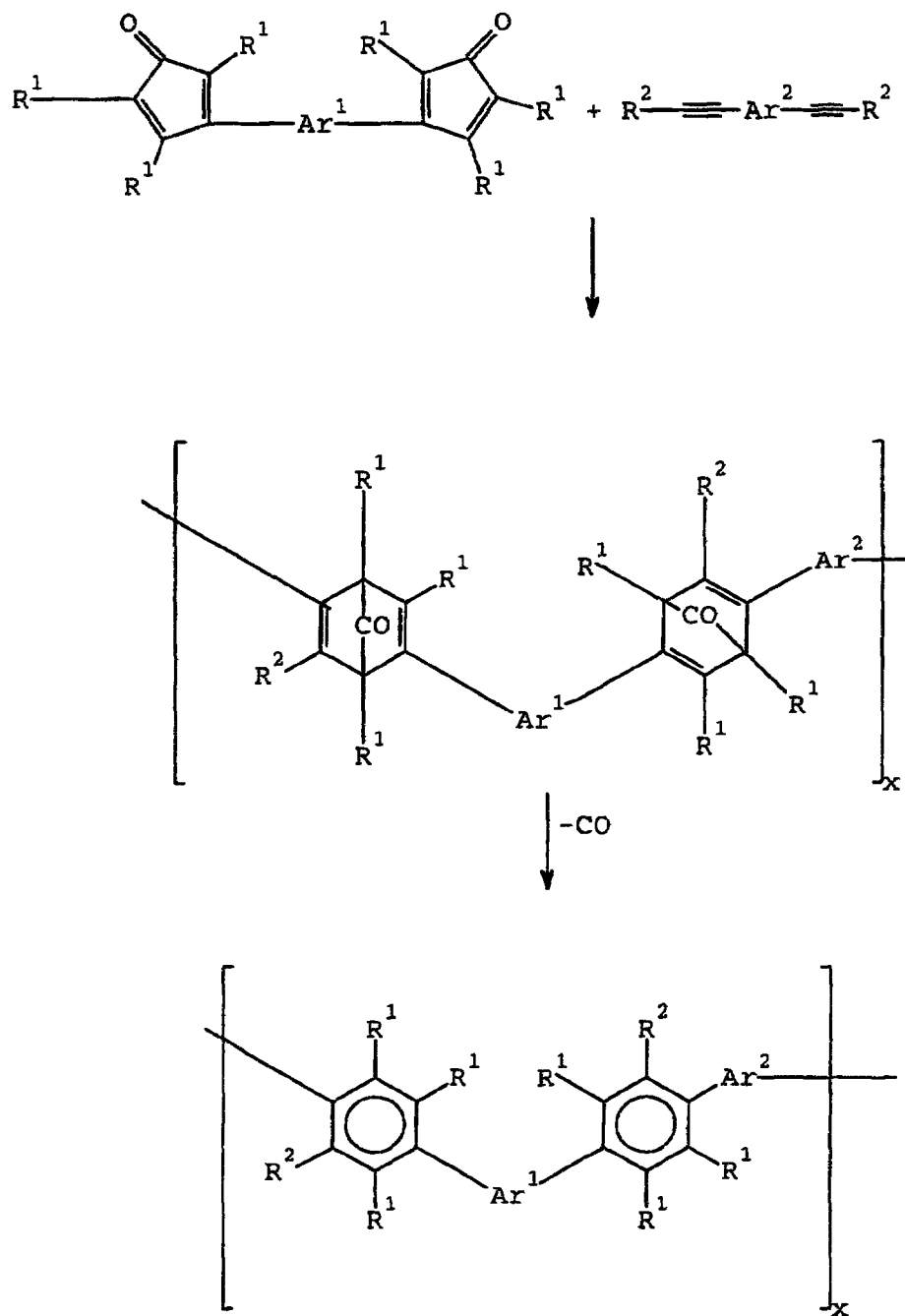
A feature of a preferred embodiment of the invention is the halting of the polymerization reaction prior to the reaction of all the cyclopentadienone moieties. The oligomer may then be applied to a surface prior to advancing the polymerization to react the balance of the cyclopentadienone moieties. In such an oligomerized state the oligomer may planarize and gap fill when applied to a patterned surface. Preferably, at least ten percent of the cyclopentadienone moieties are unreacted. Most preferably, at least twenty percent of the cyclopentadienone moieties are unreacted. One may determine the percentage of unreacted cyclopentadienone moieties by spectral analysis. The cyclopentadienone moiety is highly colored in the visible spectrum with a distinct red or purple color which fades as the cyclopentadienone moieties react.

Planarize, as used herein, means that an isolated feature may be planarized by seventy percent or more, preferably by eighty percent or more and most preferably by ninety percent or more. The percentage or degree of planarization is calculated from the equation:

$$\text{Percent Planarization} = (1 - t_f/t_m) \times 100$$

when a layer of oligomer is coated over an isolated square line, one micrometer wide and one micrometer high at an average thickness of two microns and t_f is the height of the oligomer or polymer over the feature above the average height of the oligomer or polymer and t_m is the height of the feature (one micrometer). Use of this definition is illustrated, for example, in Proceedings of IEEE, Vol. 80, No. 12, December, 1992, at page 1948.

While not being bound by theory, the preparation of the polyphenylene polymer can be represented generally as follows:



wherein R¹, R², Ar¹, Ar² and x are as defined previously.

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Furthermore, while not specifically indicated in the structures, some of the carbonyl-bridged species may be present in the oligomers prepared, depending on the specific monomer and reaction conditions used. Upon further heating, the carbonyl bridging species will be essentially fully converted to the aromatic ring system. When more than one acetylene-containing monomer is used, the oligomers and polymers formed are random,

while the structures as drawn may suggest blocks are formed. The Diels Alder reaction between the cyclopentadienone and acetylene functionality can take place to form either a para- or meta- attachment on the phenylated ring.

Any inert organic solvent which can dissolve the monomers to the appropriate degree and can be heated to the appropriate polymerization temperature either at atmospheric, subatmospheric or superatmospheric pressure could be used. Examples of suitable solvents include mesitylene, pyridine, triethylamine, N-methylpyrrolidinone (NMP), methyl benzoate, ethyl benzoate, butyl benzoate, cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclohexylpyrrolidinone, and ethers or hydroxy ethers such as dibenzylethers, diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, dipropylene glycol dimethyl ether, propylene glycol phenyl ether, propylene glycol methyl ether, tripropylene glycol methyl ether, toluene, mesitylene, xylene, benzene, dipropylene glycol monomethyl ether acetate, dichlorobenzene, propylene carbonate, naphthalene, diphenyl ether, butyrolactone, dimethylacetamide, dimethylformamide and mixtures thereof. The preferred solvents are mesitylene, N-methylpyrrolidinone (NMP), gamma-butyrolactone, diphenylether and mixtures thereof.

Alternatively, the monomers can be reacted in one or more solvents at elevated temperature and the resulting solution of oligomers can be cooled and formulated with one or more additional solvents to aid in processing, for example. In another approach, the monomers can be reacted in one or more solvents at elevated temperature to form oligomers which can then be isolated by precipitation into a non-solvent or by some other means of solvent removal to give essentially solvent-free oligomers. These isolated oligomers can then be redissolved in one or more different solvents and the resultant solutions can be used for processing.

The conditions under which the polymerization reaction is most advantageously conducted are dependent on a variety of factors, including the specific reactants and solvent. In general, the reaction is conducted under a non-oxidizing atmosphere such as a blanket of nitrogen or other inert gases. The reaction can be conducted neat (without solvent or other diluents). However, in order to ensure homogeneous reaction mixtures and to moderate exothermic reactions at such temperatures, it is often desirable to use inert organic solvents, such as those mentioned previously, for the reactants.

The time and temperature most advantageously employed will vary depending on the specific monomers employed, particularly their reactivity, the specific oligomer or polymer desired, and the solvent. In general, the reaction to form the oligomers is conducted at a temperature of from 150°C to 250°C and for a time of from 60 minutes to 48 hours. At

this point the oligomers may be isolated from the reaction mixture or used as is in the coating of a surface. Additional chain extension (advancement) may be conducted at a temperature of from 100°C to 475°C, preferably from 200°C to 450°C and for a time of from 1 minute to 10 hours, more preferably from 1 minute to 1 hour. An uncured or cured polymer may be
5 used for coating a surface by casting from a solvent. While such a polymer may not gap fill or planarize sufficiently, it may still be useful in a damascene process.

The concentrations at which the monomers are most advantageously employed in the organic liquid reaction medium are dependent on a variety of factors including the specific monomers and organic liquid employed and the oligomer and polymer
10 being prepared. In general, the monomers are employed in a cyclopentadienone to acetylene stoichiometric ratio of from 1:1 to 1:3, preferably at a 1:1 to 1:2 ratio.

The oligomer or polymer can be directly cast as a film, applied as a coating or poured into a non-solvent to precipitate the oligomer or polymer. Water, methanol, ethanol and other similar polar liquids are typical non-solvents which can be used to precipitate the
15 oligomer. Solid oligomer or polymer may be dissolved and processed from a suitable solvent. If the oligomer or polymer is obtained in solid form, it may be further processed using conventional compression molding techniques or melt spinning, casting or extrusion techniques provided the solid precursor has a sufficiently low glass transition temperature.

More commonly, the oligomer or polymer is processed directly from the
20 organic liquid reaction solution and the advantages of the present invention are more fully realized in that instance. Since the oligomer or polymer is soluble in the organic liquid reaction medium, the organic solution of the oligomer can be cast or applied and the solvent evaporated. Molecular weight increases (chain extension or advancement), and in some examples, crosslinking, to form the final polymer, occurs upon subsequent exposure to a
25 sufficiently high temperature.

The polymer of this invention may be used as one or more of the insulating or dielectric layers in single or multiple layer electrical interconnection architectures for integrated circuits, multichip modules, or flat panel displays. The polymer of the invention may be used as the sole dielectric in these applications or in conjunction with other organic
30 polymers or inorganic dielectrics, such as silicon dioxide, silicon nitride, or silicon oxynitride.

For example, coatings of oligomers and polymers of the invention, such as an electrically insulating coating used to fabricate interconnect structures on an electronic wafer, are easily prepared by spin-casting a film of, or otherwise coating a substrate with, the organic liquid solution of the oligomer or polymer and then evaporating the solvent and
35 exposing the oligomer or polymer to temperatures sufficient to advance the oligomer or

polymer to higher molecular weight, and in the most preferred examples, to a crosslinked polymer with high glass transition temperature.

The polymers of the present invention are particularly useful as a low dielectric constant insulating material in the interconnect structure of an integrated circuit, such as those fabricated with silicon or gallium arsenide. An integrated circuit would typically have multiple layers of metal conductors separated by one or more insulating materials. The polymer material of this invention can be used as insulation between discrete metal conductors in the same layer, and/or between conductor levels of the interconnect structure. The polymers of the present invention can also be used in combination with other materials, such as SiO_2 or Si_3N_4 , in a composite interconnect structure. For example, the oligomers and polymers of the invention may be used in the process for making integrated circuit devices taught in U.S. Patent 5,550,405; U.S. Patent 5,591,677 and Hayashi et al., 1996 Symposium on VLSI Technology Digest of Technical Papers, pg 88-89. The oligomers and polymers of the invention may be substituted for the BCB or other resin disclosed in the process disclosed.

The oligomer, uncured polymer or polymer of the invention may be used as a dielectric in the above taught processes or similar processes to fabricate an integrated circuit article comprising an active substrate containing transistors and an electrical interconnect structure containing patterned metal lines separated, at least partially, by layers or regions of the composition of the invention.

The polymers of the present invention are also useful to planarize materials such as silicon wafers used in semiconductors to allow the production of smaller (higher density) circuitry. To achieve the desired planarity, a coating of the oligomer or polymer is applied from solution such as by spin coating or spray coating, to flow so as to level any roughness on the surface of the substrate. These methods are illustrated by such references as Jenekhe, S.A., *Polymer Processing to Thin Films for Microelectronic Applications in Polymers for High Technology*, Bowden et al. ed., American Chemical Society 1987, pp. 261-269.

In the fabrication of microelectronic devices, relatively thin defect-free films, generally from 0.01 to 20, preferably from 0.1 to 2 micrometer thickness, can be deposited on a surface of a substrate for example silicon, silicon-containing materials, silicon dioxide, alumina, copper, silicon nitride, aluminum nitride, aluminum, quartz, and gallium arsenide. Coatings are conveniently prepared from solutions of an oligomer having a molecular weight, for example, of 3000 M_n or less and 5200 M_n or less, in a variety of organic solvents such as xylene, mesitylene, NMP, gamma-butyrolactone and n-butyl acetate. The dissolved oligomer or polymer can be cast onto a substrate by common spin and spray coating techniques. The

thickness of the coating may be controlled by varying the percent solids, the molecular weight, and thus the viscosity of the solution as well as by varying the spin speed.

The polyphenylene oligomer or polymer in this invention may be applied either by dip coating, spray coating, extrusion coating, or more preferably by spin coating. For all cases, the environment around the substrate and coating prior to cure may be controlled with respect to temperature and humidity. In particular, NMP may absorb water from the water vapor in the ambient air. When dissolved in NMP, one should protect the solution from moist air and cast the film in a low humidity environment. When using NMP as the solvent, preferably, the relative humidity is controlled at less than thirty percent and the temperature is controlled at 27°C or greater. The coating may be cured after application either with one or more hot plates, an oven, or a combination of these tools.

Adhesion promoters, such as those based on silane chemistry, may be applied to the substrate prior to the application of the polyphenylene oligomer or polymer solution, or added directly to the solution.

The oligomers and polymers of the present invention can be used in either a "damascene" metal inlay or subtractive metal patterning scheme for fabrication of integrated circuit interconnect structure. Processes for fabricating damascene lines and vias are known in the art. See for example U.S. Patents 5,262,354 and 5,093,279.

Patterning of the material may be done with typical reactive ion etch procedures using oxygen, argon, nitrogen, helium, carbon dioxide, fluorine containing compounds, or mixtures of these and other gases, using a photoresist "softmask", such as an epoxy novolac, or a photoresist in combination with an inorganic "hardmask" such as SiO₂, Si₃N₄, or metal.

The oligomers and polymers may be used in conjunction with Al, Al alloys, Cu, Cu alloys, gold, silver, W, and other common metal conductor materials (for conductive lines and plugs) deposited by physical vapor deposition, chemical vapor deposition, evaporation, electroplating, electroless deposition, and other deposition methods. Additional metal layers to the basic metal conductors, such as tantalum, titanium, tungsten, chromium, cobalt, their alloys, or their nitrides, may be used to fill holes, enhance metal fill, enhance adhesion, provide a barrier, or modify metal reflectivity.

Depending on the fabrication architecture, either metal or the dielectric material of this invention may be removed or planarized using chemical-mechanical polishing techniques.

Multichip modules on active or passive substrates such as silicon, silicate glass, silicon carbide, aluminum, aluminum nitride, or FR-4, may be constructed with the polyphenylene polymer of this invention as a dielectric material.

Flat panel displays on active or passive substrates such as silicon, silicate glass, silicon carbide, aluminum, aluminum nitride, or FR-4, may be constructed with the polyphenylene polymer of this invention as a dielectric material.

5 The oligomers and polymers of the present invention may further be used as protective coatings on integrated circuit chips for protection against alpha particles. Semiconductor devices are susceptible to soft errors when alpha particles emitted from radioactive trace contaminants in the packaging or other nearby materials strike the active surface. An integrated circuit can be provided with a protective coating of the polymer of the present invention. Typically, an integrated circuit chip would be mounted on a substrate and
10 held in place with an appropriate adhesive. A coating of the polymer of the present invention provides an alpha particle protection layer for the active surface of the chip. Optionally, additional protection is provided by encapsulant made of, for example, epoxy or a silicone.

The polymers of the present invention may also be used as a substrate (dielectric material) in circuit boards or printed wiring boards. The circuit board made up of
15 the polymer of the present invention has mounted on its surface patterns for various electrical conductor circuits. The circuit board may include, in addition to the polymer of the present invention, various reinforcements, such as woven nonconducting fibers, such as glass cloth. Such circuit boards may be single sided, as well as double sided or multilayer.

The polymers of the present invention may also be useful in reinforced
20 composites in which a resin matrix polymer is reinforced with one or more reinforcing materials such as a reinforcing fiber or mat. Representative reinforcing materials include fiber glass, particularly fiber glass mats (woven or non-woven); graphite, particularly graphite mat (woven or non-woven); Kevlar™; Nomex™; and glass spheres. The composites can be made from preforms, dipping mats in monomer or oligomer, and resin transfer molding
25 (where the mat is placed into the mold and monomer or prepolymer is added and heated to polymerize).

Layer(s) of the polymers of the present invention may be patterned by such means as wet-etching, plasma-etching, reactive-ion etching (RIE), dry-etching, or photo laser ablation, such as illustrated by *Polymers for Electronic Applications*, Lai, CRC Press (1989)
30 pp. 42-47. Patterning may be accomplished by multilevel techniques in which the pattern is lithographically defined in a resist layer coated on the polymeric dielectric layer and then etched into the bottom layer. A particularly useful technique involves masking the portions of oligomer or polymer not to be removed, removing the unmasked portions of oligomer or polymer, then curing the remaining oligomer or polymer, for example, thermally.

35 In addition, the oligomer of the present invention may also be employed to make shaped articles, films, fibers, and foams. In general, techniques well-known in the art

for casting oligomers or polymers from solution may be employed in the preparation of such products.

In preparing shaped polyphenylene oligomer or polymer articles, additives such as fillers, pigments, carbon black, conductive metal particles, abrasives and lubricating polymers may be employed. The method of incorporating the additives is not critical and they can conveniently be added to the oligomer or polymer solution prior to preparing the shaped article. The liquid compositions containing the oligomer or polymer, alone or also containing fillers, may be applied by any of the usual techniques (doctoring, rolling, dipping, brushing, spraying, spin coating, extrusion coating or meniscus coating) to a number of different substrates. If the polyphenylene oligomer or polymer is prepared in solid form, the additives can be added to the melt prior to processing into a shaped article.

The oligomer and polymer of the present invention can be applied to various substrates by a number of methods such as, solution deposition, liquid-phase epitaxy, screen printing, melt-spinning, dip coating, roll coating, spinning, brushing (for example as a varnish), spray coating, powder coating, plasma-deposition, dispersion-spraying, solution-casting, slurry-spraying, dry-powder-spraying, fluidized bed techniques, welding, explosion methods including the Wire Explosion Spraying Method and explosion bonding, press bonding with heat, plasma polymerization, dispersion in a dispersion media with subsequent removal of dispersion media, pressure bonding, heat bonding with pressure, gaseous environment vulcanization, extruding molten polymer, hot-gas welding, baking, coating, and sintering. Mono- and multilayer films can also be deposited onto a substrate using a Langmuir-Blodgett technique at an air-water or other interface.

When applying the oligomer or polymer of the invention from solution, specific conditions of polymerization and other processing parameters most advantageously employed are dependent on a variety of factors, particularly the specific oligomer or polymer being deposited, the conditions of coating, the coating quality and thickness, and the end-use application, with the solvent being selected accordingly. Representative solvents which can be employed are those described previously.

Substrate(s) which can be coated with the oligomer or polymer of the invention can be any material which has sufficient integrity to be coated with the monomer, oligomer or polymer. Representative examples of substrates include wood, metal, ceramics, glass, other polymers, paper, paper board cloth, woven fibers, non-woven fiber mats, synthetic fibers, Kevlar™, carbon fibers, gallium arsenide, silicon and other inorganic substrates and their oxides. The substrates which are employed are selected based on the desired application. Exemplary materials include glass fibers (woven, non-woven or strands), ceramics, metals such as aluminum, magnesium, titanium, copper, chromium, gold, silver, tungsten, stainless

steel, Hastalloy™, carbon steel, other metal alloys and their oxides, and thermoset and thermoplastic polymers such as epoxy resins, polyimides, perfluorocyclobutane polymers, benzocyclobutane polymers, polystyrene, polyamides, polycarbonates, polyarylene ethers and polyesters. The substrate can be the polymers of the present invention in cured form.

5 The substrate may be of any shape, and the shape is dependent on the end-use application. For instance, the substrate may be in the form of a disk, plate, wire, tubes, board, sphere, rod, pipe, cylinder, brick, fiber, woven or non-woven fabric, yarn (including commingled yarns), ordered polymers, and woven or non-woven mat. In each case the substrate may be hollow or solid. In the case of hollow objects, the polymer layer(s) is on
10 either or both the inside or outside of the substrate. The substrate may comprise a porous layer, such as graphite mat or fabric, glass mat or fabric, a scrim, and particulate material.

 The oligomers or polymers of the invention adhere directly to many materials such as compatible polymers, polymers having a common solvent, metals, particularly textured metals, silicon or silicon dioxide, especially etched silicon or silicon oxides, glass,
15 silicon nitride, aluminum nitride, alumina, gallium arsenide, quartz, and ceramics. However, when increased adhesion is desired, a material may be introduced to improve adhesion.

 Representative examples of such adhesion promoting materials are silanes, preferably organosilanes such as trimethoxyvinylsilane, triethoxyvinylsilane, hexamethyldisilazane $\{(\text{CH}_3)_3\text{-Si-NH-Si}(\text{CH}_3)_3\}$, or an aminosilane coupler such as γ -aminopropyltriethoxysilane, or a chelate such as aluminum monoethylacetoacetatedi-isopropylate $\{[(\text{isoC}_3\text{H}_7\text{O})_2\text{Al}(\text{OCOC}_2\text{H}_5\text{CHCOCH}_3)]\}$. In some cases, the adhesion promoter is applied from 0.01 weight percent to 5 weight percent solution, excess solution is removed, and then the polyphenylene applied. In other cases, for example, a chelate of aluminum monoethylacetoacetatedi-isopropylate, can be incorporated onto a substrate by
25 spreading a toluene solution of the chelate on a substrate and then baking the coated substrate at 350°C for 30 minutes in oxygen to form a very thin (for example 5 nanometer) adhesion promoting layer of aluminum oxide on the surface. Other means for depositing aluminum oxide are likewise suitable. Alternatively, the adhesion promoter, in an amount of, for example, from 0.05 weight percent to 5 weight percent based on the weight of the
30 monomer, can be blended with the monomer before polymerization, negating the need for formation of an additional layer.

 Adhesion can also be enhanced by surface preparation such as texturizing (for example, scratching, etching, plasma treating, or buffing) or cleaning (for example, degreasing or sonic cleaning); otherwise treating (for example, plasma, solvent, SO_3 , plasma
35 glow discharge, corona discharge, sodium, wet etching, or ozone treatments) or sand

blasting the substrate's surface or using electron beam techniques such as 6 MeV fluorine ions; electrons at intensities of 50 to 2000V; hydrogen cations at 0.2 to 500 eV to 1 MeV; helium cations at 200 KeV to 1 MeV; fluorine or chlorine ions at 0.5 MeV; neon at 280 KeV; oxygen enriched flame treatment; or an accelerated argon ion treatment.

5 For application of the oligomerized product of the reaction of 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) and 1,3,5-tris(phenylethynyl)benzene, a more preferred embodiment of the invention, a silane based adhesion promoter, containing 3-aminopropyl silane dissolved in methoxy propanol, available as VM-652 from DuPont or AP8000 from The Dow Chemical Company, is first applied to the wafer surface; spun slowly
10 to spread across the entire surface; allowed to stand for 2 seconds; and finally spun dry at 3000 rpm for 10 seconds. A solution of the oligomer is dispensed, 4 mL for a 200 mm wafer, by a high precision pump/filtration system, Millipore Gen-2, onto the wafer surface as the wafer is spun at 750 rpm. The wafer rotation is accelerated to 2000 rpm immediately following the dispense of the polymer solution and held at that spin speed for 20 seconds. A
15 continuous stream of mesitylene is applied to the backside of the wafer for 5 seconds during the dispense of the oligomer solution. After spin coating, the film is dried on a hot plate at 70°C for 20 seconds. After the dry-bake step, the 2 mm to 5 mm edge bead of the coating is removed with a continuous stream of mesitylene while the wafer is spun at 2000 rpm; either by application from the backside or directly from the top near the edge. After the edge bead
20 removal, the oligomer is further polymerized on a hot plate at 325°C for 90 seconds under a nitrogen blanket. The film is crosslinked either on a hot plate at 450°C for 2 minutes under nitrogen or in a nitrogen purged oven at 450°C for 6 minutes.

 The oligomer or polymer of the invention can be applied in combination with other additives to obtain specific results. Representative of such additives are metal-
25 containing compounds such as magnetic particles, for example, barium ferrite, iron oxide, optionally in a mixture with cobalt, or other metal containing particles for use in magnetic media, optical media, or other recording media; conductive particles such as metal or carbon for use as conductive sealants, conductive adhesives, conductive coatings, electromagnetic interference (EMI)/radio frequency interference (RFI) shielding coating, static dissipation, and
30 electrical contacts. When using these additives, the oligomer or polymer of the invention may act as a binder.

 The oligomer or polymer of the invention may also be employed as protection against the environment (that is, protective against at least one substance or force in an object's environment, including conditions of manufacture, storage and use) such as coatings
35 to impart surface passivation to metals, semiconductors, capacitors, inductors, conductors, solar cells, glass and glass fibers, quartz and quartz fibers.

The following examples are set forth to illustrate the present invention and should not be construed to limit its scope. In the examples, all parts and percentages are by weight unless otherwise indicated.

Example 1 Preparation of Cyclopentadienone Compounds and Acetylene

5 Compounds

Several cyclopentadienone compounds and acetylene compounds were prepared as described below. The structures of these compounds are set out in Table I, hereinafter.

A. 4-(4-(Phenylethynyl)phenyl)-2,3,5-triphenylcyclopentadienone

10 (Compound A)

(a) Preparation of 4-bromophenylacetyl chloride

4-Bromophenylacetic acid (100 g, 0.465 mol), thionyl chloride (300 mL) and DMF (about 2 mL) were charged to a 1-liter round bottom 3-necked flask equipped with a reflux condenser and a mechanical stirrer. The reaction mixture is heated under nitrogen to 15 50°C for 2 hours, using a charcoal scrubber for escaping gases. The thionyl chloride was evaporated and the product, 4-bromophenylacetyl chloride, was put into an addition funnel with benzene (30 mL).

(b) Preparation of 4-bromodeoxybenzoin

Benzene (200 mL) and aluminum chloride (74 g, 0.558 mol) were mixed into a 20 flask and the mixture of 4-bromophenylacetyl chloride and benzene in Step (a) was added dropwise allowing the reaction to evolve HCl. The reaction mixture was stirred at room temperature for 1 to 1.5 hours and poured into ice water. Ethyl acetate (1 L) was added to dissolve the precipitated solids. The layers were separated and the organic layer was washed successively with 1 M aqueous HCl, saturated aqueous NaHCO₃, brine and then 25 dried over Na₂SO₄. The solvent was then evaporated to give a solid material which was recrystallized from ethylacetate/hexanes to give the title compound in 84 percent yield as a yellow solid.

(c) Preparation of 4-Bromobenzil

Perchloric acid (250 mL), water (250 mL), ethylene glycol dimethyl ether 30 (glyme) (500 mL), thallium (III) nitrate trihydrate (222.0 g, 0.5 mol) and 4-bromodeoxybenzoin (68.75 g, 0.25 mol) were charged to a 2-liter round bottom 3-necked flask equipped with a reflux condenser and a mechanical stirrer. The reaction mixture was heated under nitrogen to reflux for 6 hours. After cooling to ambient temperature, methylene chloride (500 mL) was added. The resulting bilayer was decanted off the precipitated Tl(I) salts formed. The layers 35 were separated and the organic layer was washed with water, saturated aqueous NaHCO₃.

and brine, followed by recrystallization of the resulting solid from 2-propanol gives the title compound.

(d) Preparation of 4-(Phenylethynyl)benzil

4-Bromobenzil (10.0 g, 0.0346 mol), phenylacetylene (3.88 g, 0.0380 mol),
5 and $(\text{PPh}_3)_2\text{PdCl}_2$ (0.121 g, 0.0002 mol) in diethylamine (950 mL) was stirred at ambient temperature for 72 hours, followed by concentration to dryness. The residue was then taken up in methylene chloride. Standard aqueous workup followed by recrystallization from 2-propanol gives the title compound.

(e) Preparation of Compound A

10 4-(Phenylethynyl)benzil (20 g, 0.0644 mol), 1,3-diphenylacetone (14.2 g, 0.0677 mol) and ethanol (150 mL) were heated to 75°C. Potassium hydroxide (KOH) (1.8 g, 0.0322 mol), dissolved in ethanol (15 mL), was added dropwise over a 15 minute period. The reaction mixture was heated to reflux for 30 minutes, then cooled to 40°C and the precipitated product was filtered off, washed with cold ethanol
15 and dried. Recrystallization from 2-propanol gives the title compound.

B. 3,3'-(1,4-Phenylene)bis(2,4,5-triphenylcyclopentadienone)
(Compound B)

1,3-Diphenylacetone (1.23 g, 0.00584 mol), 1,4-bis(phenylglyoxaloyl)benzene, commercially available as Bis-PGB from Ken Seika Corporation (1.000 g, 0.00292 mol) and
20 ethanol (50 mL) were added to a 100 mL 3-necked round bottom flask fitted with a reflux condenser/nitrogen inlet. The reaction mixture was heated to reflux and an aqueous KOH solution (0.112 g, 0.002 mol) in water (2.25 mL) was added. Additional KOH was added until the solution turned dark and stayed dark. The mixture was refluxed for 45 minutes and then allowed to cool. A dark solid which precipitates was collected by filtration and analyzed by
25 $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, HPLC and FT-IR. All data was consistent with the formation of Compound B.

C. 4,4'-Bis(4-(phenylethynyl)phenoxy)-2,2',3,3',5,5',6,6'-octafluorobiphenyl (Compound C)

(a) Preparation of 4-Iodophenyl Acetate

30 4-Iodophenol (25.00 g, 0.114 mol) and methylene chloride (100 mL) were added to a 250-mL round bottom flask fitted with a condenser/nitrogen inlet, thermometer, and a dropping funnel. The slurry was stirred and pyridine (10.11 mL, 0.125 mol) was added via syringe. The reaction mixture was cooled to 10°C using an ice bath and acetyl chloride (8.89 mL, 0.125 moles) was added dropwise. The mixture was stirred at 10°C for 1 hour
35 then allowed to warm to room temperature and stirred for 2 hours. The reaction mixture was filtered and the filtrate washed with water four times. The organic layer was dried (MgSO_4)

and solvent removed *in vacuo* to give 27.3 g of an orange oil. NMR analysis was consistent with the structure of the desired product.

(b) Preparation of 4-(Phenylethynyl)phenyl Acetate

4-Iodophenyl acetate (50.00 g, 0.191 mol), phenylacetylene (23.40 g, 0.229 mol), and triethylamine (54 mL) were added to a 250-mL round bottom flask fitted with a condenser/nitrogen inlet, a thermometer, and a stopper. $\text{PdCl}_2(\text{PPh}_3)_2$ (0.200 g, 0.286 mmol) and PPh_3 (1.50 g, 5.73 mmol) were then added and the mixture heated to reflux. When the reaction mixture reached 40°C, CuI (0.054 g, 0.286 mmol) was added. After 2 hours, the reaction was allowed to cool. The mixture was diluted with methylene chloride and poured into water (500 mL). The aqueous layer was extracted with methylene chloride (100 mL). The combined organic layers were washed with three 300-mL portions of water, dried (MgSO_4), and filtered. The solvent was removed *in vacuo* to give 49 g of a yellow solid. The material was recrystallized from hexanes to give light yellow crystals, mp 104.5°C to 105.5°C.

(c) Preparation of 4-(Phenylethynyl)phenol

4-(Phenylethynyl)phenyl acetate (60.6 g, 0.256 moles), 20 percent aqueous sodium hydroxide (400 mL), and tetrahydrofuran (400 mL) were added to a 2-L Erlenmeyer flask and stirred at room temperature for 5 hours. The mixture was acidified with glacial acetic acid (120 mL) until a pH of 7 was reached. The aqueous layer was removed and extracted with tetrahydrofuran. The organic layers were combined and concentrated on a rotovap to give a tan solid. The solid was heated with hexanes (700 mL) on a steam bath and the hot solution decanted from the solid. This was repeated with a second volume of hexanes (700 mL). A white solid crystallizes from the hexane solution upon cooling and was isolated by filtration and dried *in vacuo* to give 18 g of a white solid, mp 126°C to 127°C. NMR analysis was consistent with the structure of the desired material.

(d) Preparation of Compound C

Decafluorobiphenyl (5.00 g, 14.96 mmol), 4-(phenylethynyl)phenol (5.81 g, 29.93 mmol), potassium carbonate (16.54 g, 0.1197 mol), and dimethylacetamide (150 mL) were added to a 250-mL round bottom flask fitted with a condenser/nitrogen inlet, a thermometer, and a stopper. The mixture was stirred and heated to 70°C for 16.5 hours. The reaction mixture was filtered to remove solids. The filtrate was added to water (500 mL) and extracted with methylene chloride. Brine was added to break an emulsion and the organic layer was separated and washed with water twice, then filtered through a plug of silica gel. Solvent was removed *in vacuo* leaving an oil. Methanol was added, forming a white solid which was isolated by filtration and dried *in vacuo*. NMR spectra were consistent with the structure of the title compound.

D. 4-(4-Ethynylphenyl)-2,3,5-triphenylcyclopentadienone(Compound D)

Compound D was prepared as in Example 1A using trimethylsilylacetylene in place of phenylacetylene followed by removal of the trimethylsilyl protecting group using a dilute base.

E. 3,4-Bis-(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone (Compound E)(a) Preparation of 4,4'-Dibromobenzoin

A solution of 4-bromobenzaldehyde (25.0 g, 0.135 mol), 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (1.70 g, 0.0068 mol) and triethylamine (4.10 g, 0.0405 mol) in ethanol (125 mL) was stirred at room temperature for 60 hours. The reaction mixture was concentrated to dryness, then taken up in CH_2Cl_2 (150 mL), washed with 1 M HCl and saturated aqueous NaHCO_3 and dried (Na_2SO_4), then concentrated, giving 25.2 g (100 percent) of a viscous yellow oil which solidifies upon standing at room temperature.

^1H NMR (CDCl_3) δ 7.73 (d, $J=8.5$ Hz, 2H), δ 7.52 (d, $J=8.5$ Hz, 2H), 7.44 (d, $J=8.2$ Hz, 2H), 7.17 (d, $J=8.2$ Hz, 2H) ^{13}C NMR (CDCl_3) δ 197.33, 137.56, 132.33, 132.13, 131.90, 130.43, 129.46, 129.31, 122.93, 75.68.

(b) Preparation of 4,4'-Dibromobenzil

A solution of 4,4'-dibromobenzoin (20.2 g, 0.055 mol), ammonium nitrate (4.6 g, 0.0575 mol) and copper(II) acetate (0.100 g, 0.0005 mol) in 80 percent aqueous acetic acid (200 mL) was heated at reflux for three hours. The reaction mixture was cooled to room temperature and the product which crystallized out was filtered off, washed with ethanol and dried, giving 13.0 g (64 percent) of product as a light yellow solid, mp 226°C to 228°C .

^1H NMR (CDCl_3) δ 7.83 (d, $J=8.5$ Hz, 4H), 7.66 (d, $J=8.5$ Hz, 4H); ^{13}C NMR (CDCl_3) δ 192.25, 132.44, 131.45, 131.22, 130.7.

(c) Preparation of 4,4'-Bis(phenylethynyl)benzil

A solution of 4,4'-dibromobenzil (15.8 g, 0.0431 mol), phenylacetylene (5.06 g, 0.0495 mol), $(\text{PPh}_3)_2\text{PdCl}_2$ (0.151 g, 0.0002 mol) and CuI (0.820 g, 0.0043 mol) in diethylamine (150 mL) was heated at reflux overnight. The reaction mixture was concentrated to dryness, then taken up in CH_2Cl_2 (150 mL), washed with 1 M HCl, 10 percent $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$, brine and dried (Na_2SO_4), then concentrated. Crystallization from 2-propanol gives 7.92 g (45 percent) as a light tan solid, mp 168°C to 170°C . ^1H NMR (CDCl_3) δ 7.97 (d, $J=8.2$ Hz, 4H), 7.64 (d, $J=8.2$ Hz, 4H), 7.55 (m, 4H), 7.37 (m, 6H); ^{13}C NMR (CDCl_3) δ 193.03, 132.46, 132.03, 131.82, 130.21, 129.84, 129.06, 128.47, 122.37, 94.28, 88.55.

(d) Preparation of Compound E

A solution of KOH (0.34 g, 0.0061 mol) in ethanol (5 mL) was added dropwise to a solution of 4,4'-bis(phenylethynyl)benzil (5.0 g, 0.0122 mol) and 1,3-diphenylacetone (2.69 g, 0.0128 mol) in ethanol (75 mL) at 75°C. The resulting solution was heated at reflux for one hour, cooled to room temperature and the precipitate filtered off and dried. Digestion of the product from boiling ethanol gives 5.26 g product (74 percent) as a brick red solid: m.p. 222°C (DSC); ¹H NMR (CDCl₃) δ 7.5 (bd, J=3.6 Hz, 4H), 7.34 (m, 5H), 7.25 (bs, 5H), 6.93 (d, J=8.0 Hz, 4H); ¹³C NMR (CDCl₃) δ 199.02, 152.72, 132.31, 131.14, 130.83, 129.93, 129.67, 128.99, 128.04, 127.93, 127.71, 127.28, 125.31, 123.12, 122.46, 90.60, 88.71; MS (EI) 585 (28), 584 (M⁺, 56), 556 (19), 378 (36), 278 (100).

F. 3,4-Bis-(3-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone (Compound F)(a) Preparation of 3,3'-Dibromobenzoin

Prepared as in Example 1E(a), but from 3-bromobenzaldehyde (25.0 g, 0.135 mol), 3-ethyl-5-(2-hydroxyethyl)-4-methylthiazolium bromide (1.70 g, 0.0068 mol), and triethylamine (4.10 g, 0.0405 mol) in ethanol (125 mL), giving 24.8 g (99 percent) of a viscous yellow oil. ¹H NMR (CDCl₃) δ 8.04 (s, 1H), 7.75 (d, J=7.8 Hz, 1H), 7.61 (d, J=8.0 Hz, 1H), 7.47 (s, 1H), 7.26-7.15 (m, 4H), 5.87 (s, 1H); ¹³C NMR (CDCl₃) δ 196.96, 140.48, 136.86, 134.94, 131.93, 131.86, 130.69, 130.63, 130.26, 127.57, 126.33, 123.19, 75.76.

(b) Preparation of 3,3'-Dibromobenzil

Prepared as in Example 1E(b), but from 3,3'-dibromobenzoin (24.8 g, 0.067 mol), ammonium nitrate (5.63 g, 0.070 mol) and copper(II) acetate (0.12 g, 0.0007 mol) in 80 percent aqueous acetic acid (200 mL), giving 17.0 g (69 percent) product as a light yellow solid. ¹H NMR (CDCl₃) δ 8.12 (s, 2H), 7.88 (d, J=7.8 Hz, 2H), 7.79 (d, J=7.9 Hz, 2H), 7.40 (dd, J=8.0, 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 191.58, 137.87, 134.27, 132.53, 130.60, 128.59, 123.39.

(c) Preparation of 3,3'-Bis(phenylethynyl)benzil

A solution of 3,3'-dibromobenzil (5.0 g, 0.0136 mol) and phenylacetylene (3.47 g, 0.0340 mol) in triethylamine (30 mL) was deaerated by bubbling nitrogen through the solution for ten minutes. (PPh₃)₂PdCl₂ (0.067 g, 0.0001 mol) was then added, and the reaction mixture heated at reflux overnight. The mixture was concentrated to dryness, then taken up in CH₂Cl₂ (100 mL), washed sequentially with 1 M HCl, saturated aqueous NaHCO₃ and dried (Na₂SO₄), then concentrated, giving 3.67 g (66 percent) product as a white solid: m.p. 144°C to 145°C; ¹H NMR (CDCl₃) δ 8.12 (s, 2H), 7.96 (d, J=7.9 Hz, 2H), 7.81 (d, J=7.7

Hz, 2H), 7.52 (m, 6H), 7.36 (m, 6H); ^{13}C NMR (CDCl_3) δ 192.83, 137.40, 132.82, 131.52, 129.04, 128.58, 128.25, 124.50, 122.37, 91.11, 87.62.

(d) Preparation of Compound F

A solution of KOH (0.25 g, 0.0045 mol) in ethanol (5 mL) was added dropwise to a solution of 3,3'-bis(phenylethynyl)benzil (3.67 g, 0.0089 mol) and 1,3-diphenylacetone (2.07 g, 0.0098 mol) in ethanol (100 mL) at 75°C. The resulting solution was heated at reflux for one hour, then cooled to room temperature. The resulting precipitate was filtered off and dried. Digestion of the product from boiling ethanol gives 2.0 g (38 percent) product as a dark red solid: m.p. 208°C (DSC). ^1H NMR (CDCl_3) δ 7.45 (bm, 6H), 7.31-7.21 (bm, 20H), 6.9 (d, $J=7.9$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 199.38, 152.83, 132.87, 131.48, 131.25, 131.12, 129.80, 129.60, 128.53, 127.99, 127.92, 127.84, 127.70, 127.29, 125.03, 122.96, 122.47, 90.60, 88.71.

G. 1,3,5-Tris(phenylethynyl)benzene (Compound G)

Triethylamine (375 g), triphenyl phosphine (4.7865 g), palladium acetate (1.0205 g), and N,N-dimethyl formamide (2000 mL) were charged to a 5 liter 3-necked round bottom flask equipped with a thermocouple, an overhead mechanical stirrer, a condenser, an addition funnel, and a heating mantle with a temperature controller. This mixture was stirred for 5 minutes to dissolve the catalyst. Then diethylhydroxylamine (5 g), 1,3,5-tribromobenzene (190 g) and phenylacetylene (67.67 g) were added. The reactor was purged with nitrogen for 15 minutes, and then heated to 70°C while maintaining a nitrogen atmosphere. After heating at 70°C for 30 minutes, phenylacetylene (135.33 g) was slowly added dropwise over a period of about 1 hour, and the temperature increased to 80°C. Heating was continued an additional nine hours. The reaction was then cooled to room temperature and water (1 liter) was added which precipitates crude product. The product was filtered, washed three times with 500 mL portions of water, then once with 500 mL of cyclohexane. The crystals were vacuum dried at 75°C overnight to give 226.40 g (99.1% yield) that was 97.25 area % pure by gas chromatography. The crystals were dissolved in toluene (1800 mL), refiltered through silica gel, and the solvent removed on a rotary evaporator to give 214.2 g (94.2% yield) that was 99.19 area % pure by gas chromatography. The residue was then recrystallized from a mixture of toluene (375 mL) and 2-propanol (696 mL). The white crystals were filtered, rinsed with a mixture of toluene (100 mL) and 2-propanol (400 mL), and vacuum dried at 75°C overnight to give 1,3,5-tris(phenylethynyl)benzene (190.0 g, 83.91 percent yield) that was 99.83 area % pure by gas chromatography. Additional recrystallizations from toluene/isopropanol gives material of acceptable organic and ionic purity.

H. 4,4'-Bis(phenylethynyl)diphenyl Ether (Compound H)

To a 1-liter 3-necked round bottom flask with a thermocouple well equipped with an overhead mechanical stirrer, a condenser, and a heating mantle with a temperature controller were charged triethylamine (111.5 g), triphenyl phosphine (1.158 g), palladium acetate (0.2487 g), diethylhydroxylamine (1.24 g), 4,4'-dibromodiphenyl ether (68.6 g), phenylacetylene (67.74 g), N,N-dimethyl formamide (136 mL) and 72 mL of water. The reactor was purged with nitrogen for 15 minutes, and then heated to 90°C while maintaining a nitrogen atmosphere for 19 hours. The reaction was then cooled to room temperature and water (80 mL) was added. The crude product was filtered and the solids rinsed once with a 120 mL portion of toluene and four times with 160 mL portions of water to give, upon drying overnight under vacuum, 66.37 g (85.6% yield) of fine white needles of 4,4'-bis(phenylethynyl)diphenyl ether that were 99.64 area percent pure by gas chromatography.

I. 4,4''-Bis(phenylethynyl)-o-terphenyl (Compound I)(a) Preparation of 4,4''-Dibromo-o-terphenyl

o-Terphenyl (100 g), Fe (5 g) and CHCl_3 (475 mL) were charged to a 1-L 3-necked flask equipped with a mechanical stirrer, a condenser connected to an HBr trap and an addition funnel. The mixture was stirred and temperature was maintained by a water bath. Br_2 (47.5 mL) in CHCl_3 (150 mL) was added dropwise over a period of 2.5 hours. The mixture was stirred at room temperature for an additional two hours. GC showed 5 percent monobromo-*o*-terphenyl, 81 percent dibromo-*o*-terphenyl and 9 percent tribromo-*o*-terphenyl.

Ice and 2 N NaOH solution were added to the above solution until it was basic. The upper layer was decanted and the CHCl_3 solution washed with more water. Sodium sulfate was added to the CHCl_3 solution which was then filtered through a Buchner funnel filled with celite. Chloroform was removed. To the white solid was added 750 mL of glacial acetic acid and the slurry was heated with a water bath at 95°C. About half of the solid dissolved. The hot solution was decanted into a 1000 mL beaker. The residue solid was 71 g which consisted of 1.4 percent monobromo-*o*-terphenyl, 93 percent 4,4''-dibromo-*o*-terphenyl and 6 percent 4,4',4''-tribromo-*o*-terphenyl. The acetic solution was allowed to cool to room temperature. White crystals were collected. GC shows 1 percent monobromo-*o*-terphenyl, 83 percent 4,4''-dibromo-*o*-terphenyl, and 13 percent 4,4',4''-tribromo-*o*-terphenyl. This material was used in the preparation of 4,4''-bis(phenylethynyl)-*o*-terphenyl.

(b) Preparation of Compound I

4,4''-Dibromo-*o*-terphenyl (40 g, 0.0103 mol), phenylacetylene (50 mL), triethylamine (500 mL) and pyridine (300 mL) were charged to a 1000 mL 4-necked flask equipped with a mechanical stirrer, a condenser, N_2 inlet and a thermometer. Nitrogen was used to purge the system for 20 minutes.

After the solid was dissolved, 2.783 g of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 2.538 g of CuI , and 5.545 g of PPh_3 were added. Nitrogen was bubbled through the solution with stirring for 30 minutes. Heat was turned on to reflux the mixture. Refluxing was maintained overnight. White solid forms during the reaction.

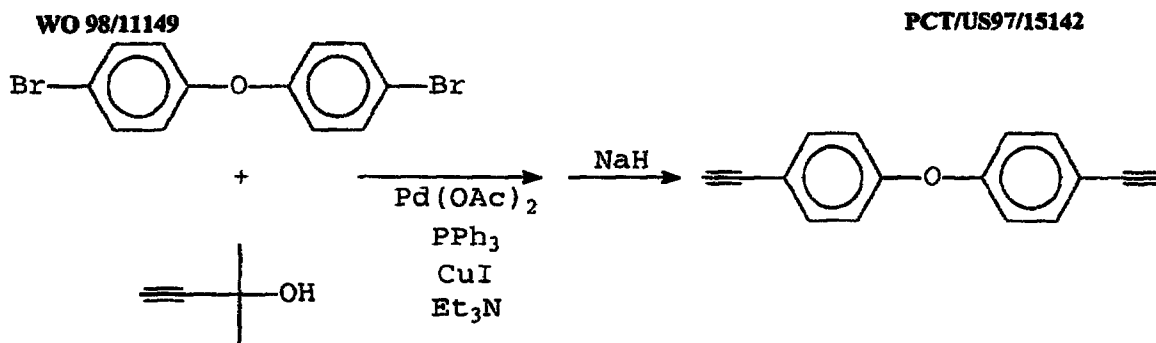
5 The solution was put into a 2-L beaker which contained ice. The flask was rinsed with water several times and poured into the beaker. The solid formed was filtered with a Buchner funnel and then washed several times with water. Toluene was used to dissolve the solid in a 2-L beaker. The upper layer was decanted into a 1-L flask. The lower layer which contains undissolved materials was rinsed with toluene and the toluene solution
10 was combined with the decanted upper layer, forming a deep brown solution. The deep brown solution was decolorized with charcoal. The solution was heated in a water bath while being stirred. Na_2SO_4 was then added.

 The solution was filtered with a sintered glass filter and the solvent was rotovapped off. The solid was dissolved in a 2-L beaker with 350 mL of hot toluene and,
15 once dissolved, 1300 mL of isopropanol was added to crystallize the solid. The 2-L beaker was put into the refrigerator overnight, the crystals were then collected, and washed with isopropanol. The yellow solid weighed 25 g. The yellow solid was washed with acetone and then crystallized twice in ethyl acetate. Yield of white flakes was 12 g.

J. 4,4'-Diethynyldiphenyl ether (Compound J)

20 A slurry of 4,4'-dibromodiphenyl ether (9.8 g, 0.030 mol), $\text{Pd}(\text{OAc})_2$ (0.05 g, 0.0002 mol), copper(I) iodide (0.15 g, 0.0008 mol) and triphenylphosphine (1.0 g, 0.0038 mol) in triethylamine (40 mL) was sparged with nitrogen for 30 minutes, while slowly heating to reflux.

2-Methyl-3-butyne-2-ol (7.6 g, 0.090 mol), which was sparged with nitrogen for 30 minutes,
25 was rapidly added to the refluxing solution over a 5 minute period. The resulting reaction mixture was heated at reflux for 14 hours, cooled to ambient temperature, and concentrated to dryness. The residue was taken up in CH_2Cl_2 , washed with water and brine, then concentrated. The residue was taken up in toluene (200 mL) and sodium hydride (0.10 g, 0.20 mol) was added. The reaction mixture was heated to reflux and approximately 100 mL
30 of the solvent was distilled off. The solution was cooled, then concentrated. The residue was taken up in CH_2Cl_2 , washed with 1 N HCl, water, saturated aqueous NaHCO_3 and brine, then dried (Na_2SO_4) and concentrated, giving a dark colored oil. The residue was filtered through a pad of silica gel, eluted with CH_2Cl_2 and concentrated, giving a viscous oil which slowly solidified upon standing. ^1H NMR (CDCl_3) δ 7.45 (d, $J=8.6$ Hz, 4 H), 6.93 (d, $J=8.7$ Hz, 4 H),
35 3.04 (s, 2 H); ^{13}C NMR (CDCl_3) δ 157.02, 133.93, 119.20, 118.94, 117.16, 83.16. The reaction scheme was as follows:



K. 3,3'-(Oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone)
(Compound K)

5 (a) Preparation of 4,4'-diphenylacetyldiphenyl ether

To a slurry of aluminum chloride (97.9 g, 0.734 mol) in methylene dichloride (200 mL) at 0°C was added, dropwise, a solution of diphenyl ether (50.0 g, 0.294 mol) and phenylacetyl chloride (102 g, 0.661 mol) in methylene chloride (50 mL), over a 30 minute period. When the addition was completed, the reaction mixture was allowed to warm to ambient temperature and stirred overnight. The reaction mixture was carefully poured, with stirring, into 1.5 kg of ice/water. Methylene chloride (1500 mL) was added to dissolve the solids and the layers were separated. The organic layer was filtered through celite, then concentrated to dryness. Recrystallization from toluene gives 110 g (92 percent) of the title compound as light tan prisms.

15 (b) Preparation of 4,4'-Bis(phenylglyoxaloyl)diphenyl Ether

Aqueous HBr (97 mL of a 48 weight percent solution) was added to a slurry of 4,4'-diphenylacetyldiphenyl ether (50.0 g, 0.123 mol) in DMSO (400 mL) and the resulting mixture was heated to 100°C for two hours, then cooled to ambient temperature. The reaction mixture was partitioned between toluene (500 mL) and water (750 mL). The organic layer was washed with water (3 X 250 mL), followed by washing with brine, and concentration to give a viscous, bright yellow oil which solidified upon standing at ambient temperature. Recrystallization from ethanol gives 35.9 g (67 percent) of the title compound as bright yellow cubes.

(c) Preparation of Compound K

To a nitrogen purged 5-L Morton flask equipped with a thermocouple, reflux condenser with nitrogen inlet, mechanical stirrer, and addition funnel was added, 195.4 g (0.4498 mol, 1.0 eq) 4,4'-bis(phenylglyoxaloyl)diphenyl ether, 193.9 g diphenylacetone (0.9220 mol, 2.05 eq), and 2.5 L deoxygenated ethanol. The mixture was heated to reflux, at which point a homogeneous solution was attained, and the solution was sparged with nitrogen for 30 minutes. To the addition funnel was added a solution containing 25.2 g KOH (0.4498 mol, 1.0 eq), 200 mL ethanol, and 25 mL water. The temperature was reduced to 74°C and the KOH solution was added rapidly over 5 minutes. An exothermic reaction was quickly established and maintained reflux until three quarters of the solution was added whereafter the temperature begins to decrease. A dark purple color was observed immediately upon addition of base and solid was observed before addition was complete. After complete addition, the heterogeneous solution was heated at strong reflux for 15 minutes and much solid product was formed. The mixture was allowed to cool to 25°C and 29.7 g glacial acetic acid (0.4948 mol, 1.1 eq.) was added and stirred for 30 minutes. The crude product was isolated by filtration and washed in the filter funnel with, 1 L water, 3 L EtOH, 2 L MeOH, and dried for 12 hours at 60°C to 90°C under vacuum giving 323 g (92 percent) crude DPO-CPD which was 94 percent pure by LC. The crude material was dissolved in HPLC grade methylene chloride (10 weight percent), transferred to a 5-L Morton flask equipped with a bottom flush valve and mechanical stirrer, and washed vigorously for 10 to 90 minutes, 2 to 7 times with equal volume portions of low ionic water. The CH₂Cl₂ solution was then flashed through a 5 cm column containing 75 g of silica gel in CH₂Cl₂. The column was washed with an additional 1 L CH₂Cl₂ at which point the filtrate was essentially clear. The solution was evaporated to dryness and re-dissolved in THF and evaporated again to remove the bulk of the residual methylene chloride. The powder was transferred to a 5 L flask equipped with addition funnel and Friedrichs reflux condenser, and dissolved (0.07 to 0.12 g/mL) in deoxygenated HPLC THF at reflux. An additional 1 L THF was then added and a nitrogen sparge tube was inserted into the solution. The solution was sparged with nitrogen for three hours and the THF was condensed at 45°C to 50°C while residual methylene chloride was removed by distillation. A distillation head was attached and 700 mL to 1 L THF was removed. The solution was then allowed to slowly cool over several hours to room temperature then cooled with an ice bath to below 10°C during which time crystallization occurs. The crystals were isolated using a 5 mm PTFE filter in a 4-L Millipore clamp-frit suction filtration flask. The crystals were then washed with 1-L MeOH and dried over night at 80°C to 90°C under vacuum giving 70 to 85 percent yield DPO-CPD with 99 percent LC purity, mp 270°C.

L. 2,4,4'-Tris(phenylethynyl)diphenyl ether (Compound L)(a) Preparation of 2,4,4'-tribromodiphenyl ether

Bromine (57.3g, 0.358 mol) was slowly added dropwise to neat stirring diphenyl ether (20.0 g, 0.118 mol) at 40°C. During the addition, the temperature was slowly raised to 60°C and the reaction was maintained at that temperature for two hours. The mixture was then heated to 70°C for 30 minutes, then cooled to ambient temperature. The mixture was taken up in CH₂Cl₂ (100 mL), washed with 10 percent aqueous Na₂CO₃, then dried (Na₂SO₄) and concentrated, giving 44.8 g (100 percent) product as a tacky oil which slowly solidified upon standing at ambient temperature.

(b) Preparation of Compound L

A slurry of 2,4,4'-tribromodiphenyl ether (44.3 g, 0.116 mol), Pd(OAc)₂ (0.182 g, 0.00081 mol), copper (I) iodide (574 g, 0.00302 mol) and triphenylphosphine (3.95 g, 0.0151 mol) in triethylamine (300 mL) was sparged with nitrogen for 30 minutes, while slowly heating to reflux.

Phenylacetylene (41.4 g, 0.406 mol), which was sparged with nitrogen for 30 minutes, was rapidly added to the refluxing solution over a 5 minute period. The resulting reaction mixture was heated at reflux for 14 hours. The solution was cooled to ambient temperature and concentrated. The residue was taken up in CH₂Cl₂, washed with 1 N HCl, water, saturated aqueous NaHCO₃ and brine, then concentrated to 100 mL volume. This solution was filtered through a pad of silica gel, eluted with methylene chloride and the resulting filtrate concentrated. The residue was crystallized from EtOAc/hexanes to give 39.0 g (73 percent) as a light tan solid, mp 123°C to 126°C. ¹H NMR (CDCl₃) δ 7.77 (bs, 1 H), 7.53-7.44 (m, 14 H), 7.34-7.26 (m, 20 H), 6.98 (dd, J=8.0, 8.0, 2 H); ¹³C NMR (CDCl₃) δ 156.81, 156.00, 136.49, 132.93, 132.57, 131.31, 131.22, 128.23, 128.10, 128.06, 127.99, 127.87, 123.04, 122.74, 122.51, 119.63, 119.09, 118.67, 117.84, 116.30, 95.05, 89.47, 88.72, 87.79, 83.87.

M. 3,3'-(1,4-Phenylene)bis(2,5-di-(4-fluorophenyl)-4-phenylcyclopentadienone)(Compound M)

1,3-Bis(4-fluorophenyl)-2-propanone (1.476 g, 0.006 mol) and 1,4-bis(phenylglyoxaloyl)benzene, available as Bis-PGB from Ken Seika Corporation (1.026 g, 0.003 mol), were dissolved in 90 mL of 1-propanol and benzyltrimethylammonium hydroxide (0.32 g, 40 percent in methanol) was added. The solution immediately turned purple. Reflux was continued for 2 hours. The mixture was cooled to room temperature and then at 0°C. Solid was collected and washed with cold methanol. Yield was 1.92 g. The solid had a metallic shiny color and melts at 316°C as measured by DSC.

1,3-Bis(4-fluorophenyl)-2-propanone was prepared following the procedure described in E. Elce, A. S. Hay, *J. Poly. Sci.: Part A: Polymer Chemistry*, 33, 1143-1151 (1995).

N. 4,4',4''-Tris(phenylethynyl)-o-terphenyl (Compound N)

5 (a) Preparation of 4,4',4''-Tribromo-o-terphenyl

o-Terphenyl (39.6 g), Fe (3.3 g) and CHCl_3 (450 mL) were charged to a 1-L 3-necked flask equipped with a mechanical stirrer, a condenser connected to an HBr trap and an addition funnel. The mixture was stirred and temperature was maintained by a water bath. Br_2 (26.5 mL) in CHCl_3 (100 mL) was added dropwise over a period of 1.5 hours. The mixture was stirred at room temperature for an additional 2 hours and then at 65°C for 2 hours. GC showed 14 percent dibromo-*o*-terphenyl, 85 percent tribromo-*o*-terphenyl and 0.7 percent tetrabromo-*o*-terphenyl.

Ice and 2 N NaOH solution were added to the solution until it was basic. The upper layer was decanted and the CHCl_3 solution was washed with more water. Sodium sulfate was added to the CHCl_3 solution which was then filtered through a Buchner funnel filled with celite. Chloroform was removed. The white solid was mixed with 750 mL glacial acetic acid and the slurry was heated with a water bath at 95°C. Yield of solid after all acetic acid was removed was 42.5 g, consisting of 11 percent 4,4''-dibromo-*o*-terphenyl, 88 percent 4,4',4''-tribromo-*o*-terphenyl and 0.6 percent tetrabromo-*o*-terphenyl. The solid was used in the preparation of 4,4',4''-tris(phenylethynyl)-*o*-terphenyl. The acetic acid solution contained 56 percent 4,4''-dibromo-*o*-terphenyl, 36 percent 4,4',4''-tribromo-*o*-terphenyl and 1.8 percent tetrabromo-*o*-terphenyl.

(b) Preparation of Compound N

4,4',4''-Tribromo-*o*-terphenyl (24.7 g, 0.053 mol), phenylacetylene (22 mL), triethylamine (280 mL) and pyridine (180 mL) were charged to a 1000-mL 4-necked flask equipped with a mechanical stirrer, a condenser, and N_2 inlet and a thermometer. Nitrogen was used to purge the system for 20 minutes.

After the solid was dissolved, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (1.113 g), CuI (1.005 g) and PPh_3 (2.218 g) were added. Nitrogen was bubbled through the solution with stirring for 30 minutes. Heat was turned on and the mixture was refluxed overnight. White solid formed during the reaction.

The solution was put into a 2-L beaker which contains ice. The flask was rinsed with water several times and poured into the beaker. The gummy solid formed was filtered with a Buchner funnel and then washed several times with water. Toluene was used to dissolve the solid in a 2-L beaker. The upper layer was decanted into a 1-L flask. The lower layer which contained undissolved materials was rinsed with toluene and the toluene

solutions were combined, forming a deep brown solution which was subsequently decolorized with charcoal. The solution was heated in a water bath while being stirred. Na_2SO_4 was then added. The solution was filtered with a sintered glass filter and the solvent was rotovapped off. The gummy solid was dissolved in a 2-L beaker with 600 mL of hot acetone. The crystals were then collected and washed with acetone. The light yellow solid weighs 11 g. The solid was crystallized twice from ethyl acetate. Yield of white powder was 8 g.

O. 1,3-Bis(phenylethynyl)benzene (Compound O)

Phenylacetylene (8.0 g, 78.3 mmol),

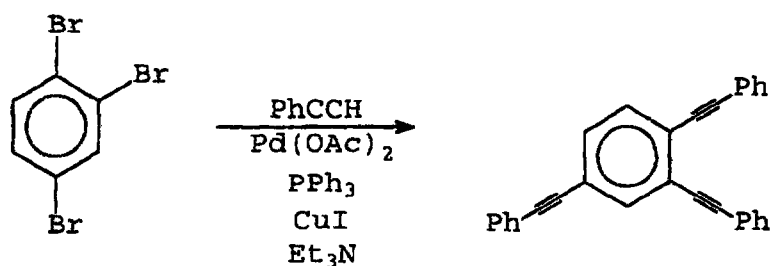
1,3-dibromobenzene (6.24 g, 26.5 mmol), bis(triphenylphosphine)palladium(II) chloride (0.557 g, 0.794 mmol), triphenylphosphine (1.11 g, 4.23 mmol), copper(I) iodide (0.503 g, 2.64 mmol), pyridine (73 mL, 0.93 mol), triethylamine (110 mL, 0.783 mol) were mixed and stirred under nitrogen for 30 minutes. The mixture was then refluxed overnight. The solution was poured into a water/ice bath. The solid which formed was collected and washed with water. The solid was dissolved in toluene and the insoluble material was filtered off. The toluene solution was decolorized with charcoal. Isopropanol was added, forming yellow crystals. The crystals were isolated by filtration and weigh 4.0 g (13.1 mmol, 50 percent yield). Melting point was 109°C (DSC). NMR and mass spectroscopic analyses were consistent with the proposed structure of 1,3-bis(phenylethynyl)benzene.

P. 1,4-Bis(phenylethynyl)benzene (Compound P)

Compound P was prepared as in Compound O except that 1,4-dibromobenzene was used instead of 1,3-dibromobenzene.

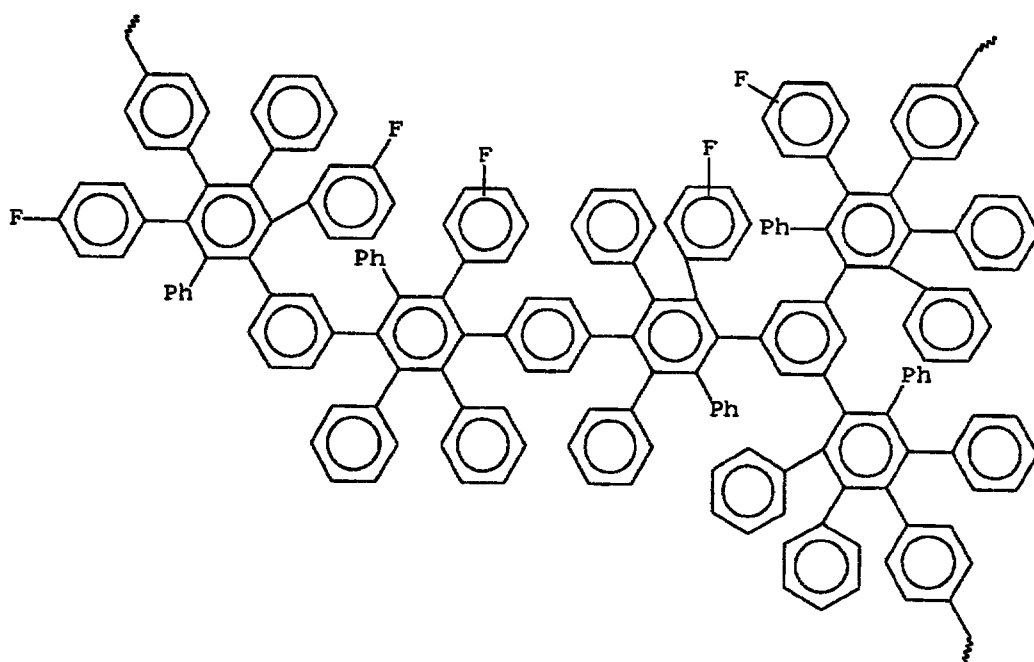
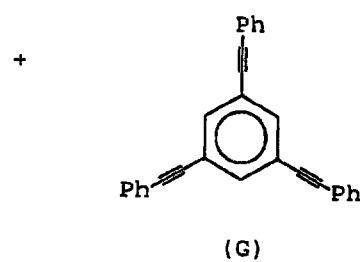
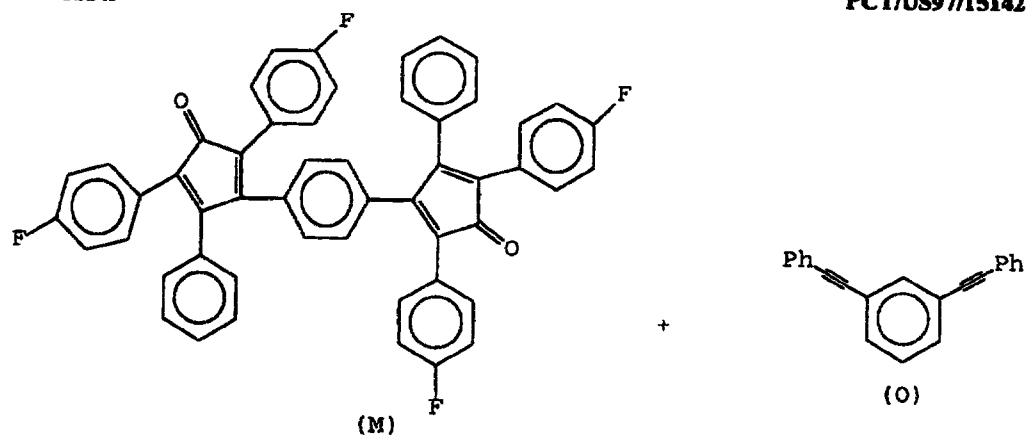
Q. 1,2,4-Tris(phenylethynyl)benzene (Compound Q)

A slurry of 1,2,4-tribromobenzene (20.0 g, 0.0635 mol) in triethylamine (250 mL) was degassed by sparging with N_2 for 30 minutes. Triphenylphosphine (2.2 g, 0.00836 mol) was added, followed by $\text{Pd}(\text{OAc})_2$ (0.100 g, 0.000445 mol) and CuI (0.315 g, 0.00165 mol), and the resulting mixture was heated to reflux. Phenylacetylene (20.1 g, 0.197 mol), which was sparged with N_2 for 30 minutes, was added dropwise over a 10 minute period. The reaction mixture was heated at reflux overnight. The reaction mixture was cooled to ambient temperature and concentrated to dryness. The residue was taken up in acetone (200 mL) and water (300 mL) was slowly added with stirring. The precipitate was filtered off, washed with methyl alcohol (500 mL), then water (200 mL) and dried, giving a light tan colored solid which was further purified by recrystallization from acetone/methanol, giving a white solid in 60 percent yield. NMR analysis was consistent with the structure of the desired material. The reaction scheme was as follows:



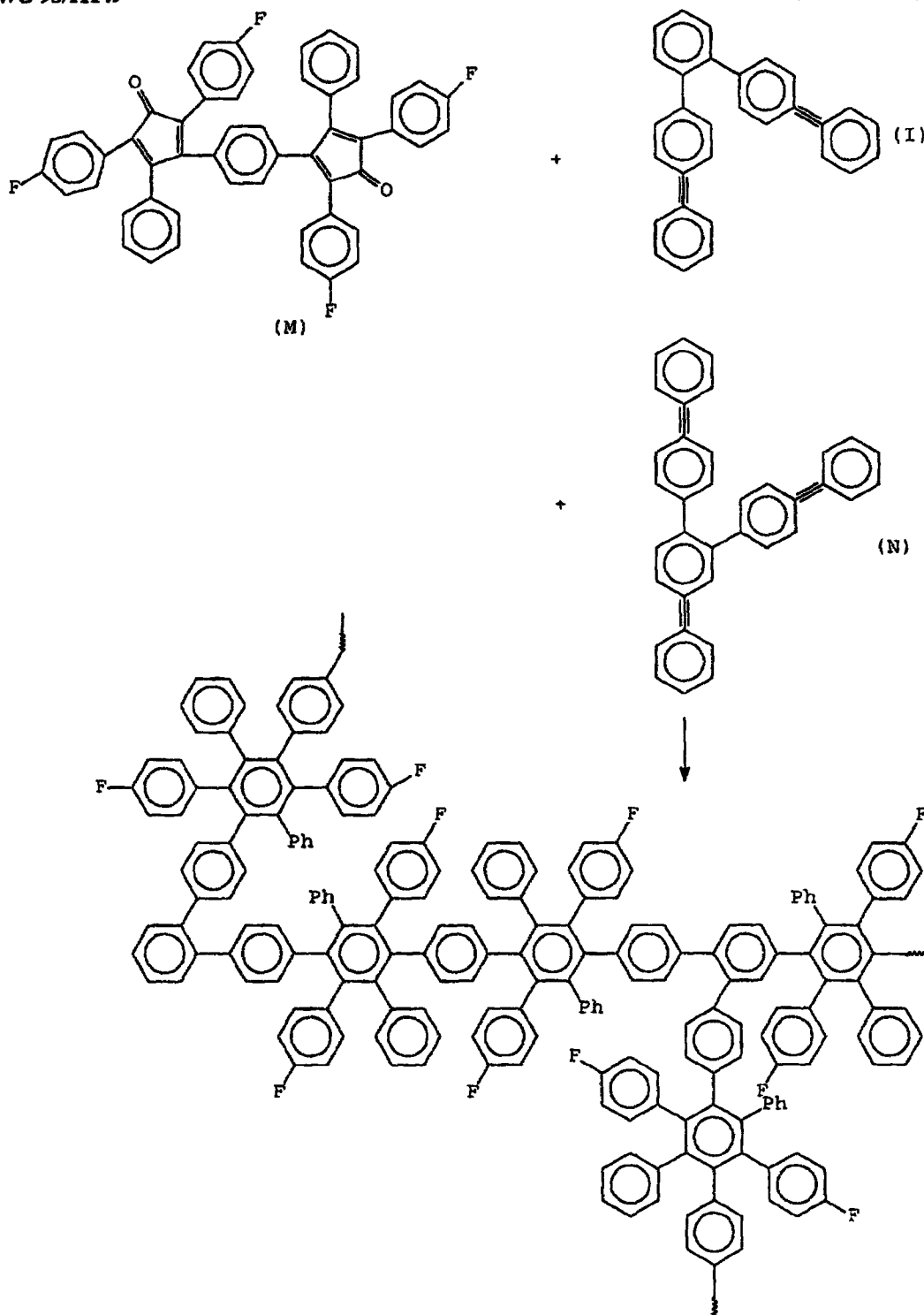
Example 2 Preparation of Polymer from Compound M and a Mixture of 1,3-bis(phenylethynyl)benzene (Compound O) and 1,3,5-tris(phenylethynyl)benzene (Compound G)

Compound (M) (316 mg, FW = 762, 0.415 mmol), Compound (O) (72 mg, FW = 278, 0.259 mmol) and Compound (G) (44 mg, 0.116 mmol) were refluxed in 1,3-diisopropylbenzene (4 mL) for 42 hours. The dark solution turned red and became viscous. The solution was spin-coated on a wafer and cured at 400°C for 1 hour, forming a film. The reaction scheme is as follows:



Example 3 Preparation of Polymer from Compound M and a Mixture of 4,4'-bis(phenylethynyl)-o-terphenyl (Compound I) and 4,4',4''-tris(phenylethynyl)-o-terphenyl (Compound N)

- Compound (M) (316 mg, 0.415 mmol), Compound (I) (107 mg, FW = 430, 0.249 mmol) and Compound (N) (88 mg, FW = 530, 0.166 mmol) were refluxed in 5 mL of 1,3-diisopropylbenzene for 48 hours. The yellow viscous solution was cooled to room temperature and spin-coated on a wafer. The polymer was cured at 400°C for 1 hour, forming a film. The reaction scheme is as follows:



Example 4 Preparation of Polymer from 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (Compound K) and 4,4'-Bis(phenylethynyl) diphenyl ether (Compound H)

5 3,3'-(Oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (15.0000 g, 0.019158 mol), 4,4'-bis(phenylethynyl)diphenyl ether (7.0974 g, 0.019158 mol), and N-

methyldipyrrolidinone (51.60 g) were added to a 250-mL round bottom flask. The flask was attached to a nitrogen inlet and the magnetically stirred solution was heated to 200°C in an oil bath. After 19.5 hours at 200°C, gel permeation chromatography indicated a M_n of 1551 and a M_w of 2383 relative to a polystyrene standard. The solution was allowed to cool and was
5 bottled. A portion of the solution was taken up in a syringe and filtered through a 1.0 micron syringe filter onto a 4" silicon wafer. The wafer was spin-coated at 2000 rpm for 60 seconds under a heat lamp which warmed the wafer. The coated wafer was then placed on a hot plate set to 90°C for several minutes. The wafer was then placed in a nitrogen purged oven where it was cured by purging at room temperature for 45 minutes then heated to 400°C at
10 10°C/minute, held at 400°C for 1 hour, then allowed to cool to room temperature. The resulting wafer was thus coated with a polyphenylene polymer. The solution, when applied to a gap fill structure with submicron gaps and cured, was found to completely fill the gaps.

Example 5 Preparation of Polymer from 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (Compound K), 4,4'-Bis(phenylethynyl) diphenyl ether (Compound H), and 1,3,5-Tris(phenylethynyl)benzene (Compound G)

To a 100-mL 3-necked round bottom flask was added 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (10.0000 g, 0.01277 moles), 4,4'-bis(phenylethynyl)diphenyl ether (2.3660 g, 0.006386 moles), 1,3,5-tris(phenylethynyl)benzene (2.4170 g, 0.006386 moles), and N-methyldipyrrolidinone (34.5
20 mL). The flask was attached to a nitrogen inlet and the magnetically stirred solution was heated to 200°C in an oil bath. After 11 hours at 200°C the solution was allowed to cool and was bottled. A portion of the solution was taken up in a syringe and filtered through a 1.0 micron syringe filter onto a 4 inch silicon wafer. The wafer was spin-coated at 2000 rpm for 60 seconds. The coated wafer was then placed on a hot plate set to 90°C for two minutes.
25 The wafer was then placed in a nitrogen purged oven where it was cured by purging at room temperature for 45 minutes then heated to 400°C at 10°C/minute, held at 400°C for 1 hour, then allowed to cool to room temperature. The resultant wafer was thus coated with a polyphenylene polymer. The solution, when applied to a gap fill structure with submicron gaps, and cured was found to completely fill the gaps. The cured polymer was insoluble in
30 N-methyldipyrrolidinone.

Example 6 Preparation of Polymer from 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (Compound K), 1,3-Bis(phenylethynyl)benzene (Compound O) and 1,3,5-Tris(phenylethynyl)benzene (Compound G)

To a 25-mL Schlenk tube was added 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (2.0000 g, 0.002554 moles), 1,3-bis(phenylethynyl) benzene (0.4740 g, 0.001703 moles), 1,3,5-tris(phenylethynyl)benzene (0.4834 g, 0.001277 moles), and N-methylpyrrolidinone (6.9 mL). The tube was attached to a nitrogen inlet and the magnetically stirred solution was heated to 200°C in an oil bath. After 20 hours at 200°C, gel permeation chromatography indicated a $M_n = 1463$ and a $M_w = 2660$ relative to a polystyrene standard. The solution was allowed to cool to room temperature and was bottled. A portion of the solution was taken up in a syringe and filtered through a 1.0 micron syringe filter onto a 4" silicon wafer. The wafer was spin-coated at 2000 rpm for 60 seconds under a heat lamp which warms the wafer. The coated wafer was then placed on a hot plate set to 90°C for two minutes. The wafer was then placed in a nitrogen purged oven where it was cured by purging at room temperature for 45 minutes, then heated to 400°C at 10°C/minute held at 400°C for 1 hour, then allowed to cool to room temperature. The resultant wafer was thus coated with a polyphenylene polymer.

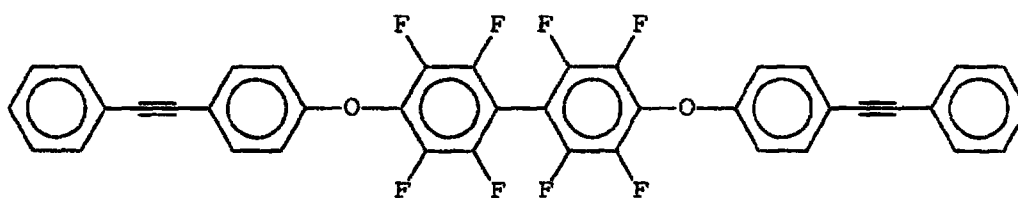
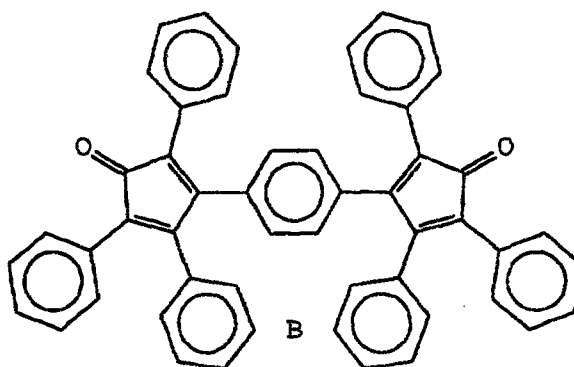
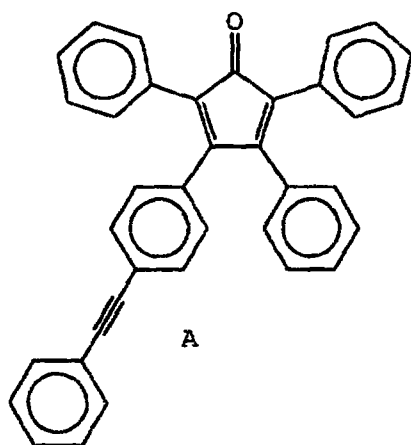
Example 7 Preparation of Oligomer Solution from 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (Compound K) and 1,3,5-Tris(phenylethynyl)benzene (Compound G)

To a Pyrex® 1-L 3-necked round bottom flask which had been rinsed with deionized water and HPLC grade acetone and dried was added low ionic 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) (100.0 g, 0.128 moles), low ionic 1,3,5-tris(phenylethynyl)benzene (48.3 g, 0.128 moles), and electronic grade N-methylpyrrolidinone (346 g). The flask was attached to a nitrogen/vacuum inlet. The magnetically stirred solution was degassed by applying vacuum and refilling with nitrogen five times. Nitrogen gas was then allowed to flow through the headspace of the flask and exit through a mineral oil bubbler. The solution was then heated to an internal temperature of 200°C. After 8.5 hours of heating the solution was allowed to cool and was transferred into a bottle made of tetrafluorethylene. Analysis of the final solution by gel permeation chromatography indicated a $M_n = 1498$ and a $M_w = 2746$ relative to a polystyrene standard. Analysis of the final solution by reverse phase chromatography indicated a residual 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) level of 1.8 weight percent. Analysis of the final solution by neutron activation indicated a sodium level of 52 ppb, a potassium level of 190 ppb, a palladium level of 90 ppb, a bromine level of 2.4 ppm, an iodine level of 0.6 ppm, and a chlorine level of 2.4 ppm.

Example 8 Coating and Curing of Oligomer Solution from Example 7.

A silane based adhesion promoter, AP8000 available from The Dow Chemical Company, was first applied, 3 mL for a 200 mm wafer, to the surface of a wafer; spun slowly to spread across the entire surface; allowed to stand for 2 seconds; and finally spun dry at 5 3000 rpm for 10 seconds. The polyphenylene oligomer solution prepared in Example 7 was applied, 4 mL for a 200 mm wafer, by a high precision pump/filtration system, Millipore Gen-2, onto the wafer surface coated with adhesion promoter as the wafer was spun at 750 rpm. The wafer rotation was accelerated to 2000 rpm immediately following the application of the oligomer solution and held at that spin speed for 20 seconds. A continuous stream of 10 mesitylene was applied to the backside of the wafer for 5 seconds during the application of the oligomer solution. After spin coating the wafer with the oligomer solution, the film was dried on a hot plate at 70°C for 20 seconds. After the dry bake step, the 2 mm to 5 mm edge bead of the coating was removed with a continuous stream of mesitylene while the wafer was spun at 2000 rpm either by application from the backside or directly from the top near the 15 edge. After the edge bead removal, the oligomer was further polymerized on a hot plate at 325°C for 90 seconds under a nitrogen blanket. The film was then crosslinked either on a hot plate at 450°C for 2 minutes under nitrogen or in a nitrogen purged oven at 450°C for 6 minutes. The film has a glass transition temperature greater than 450°C as measured by Dynamic Mechanical Analysis.

Table I



C

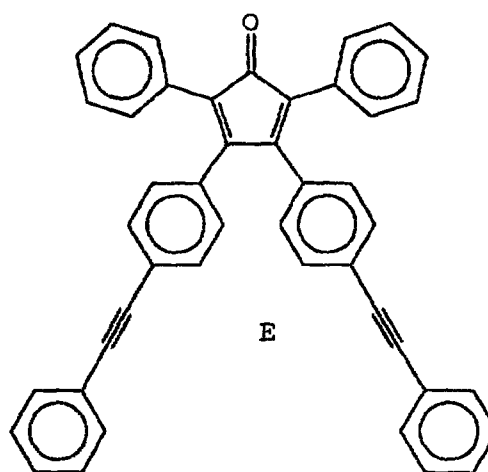
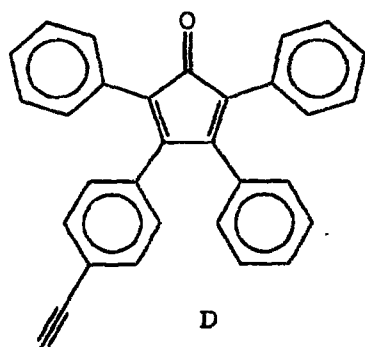


Table I (continued)

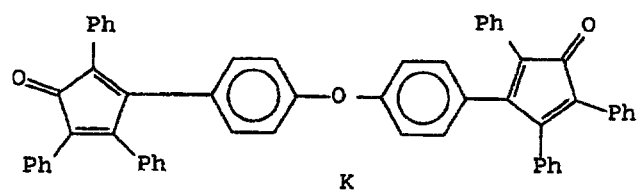
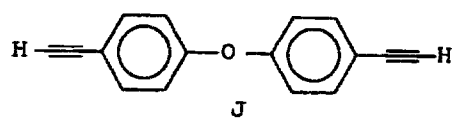
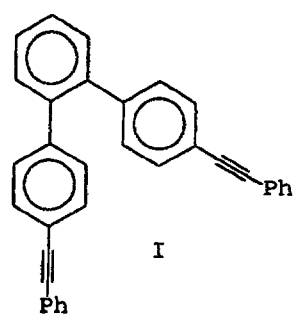
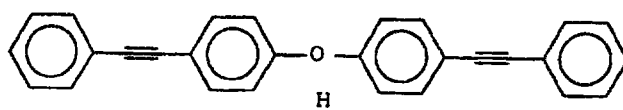
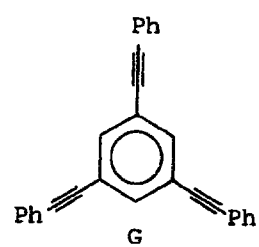
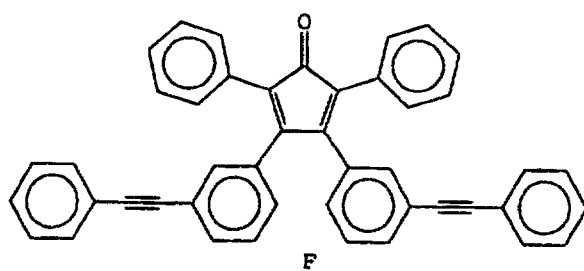
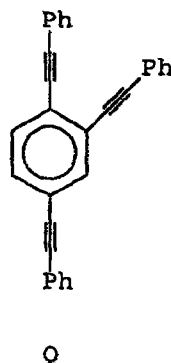
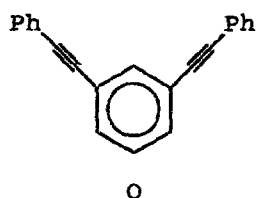
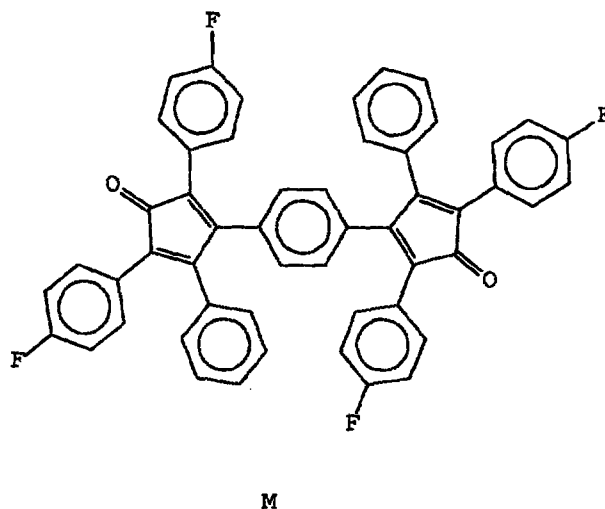
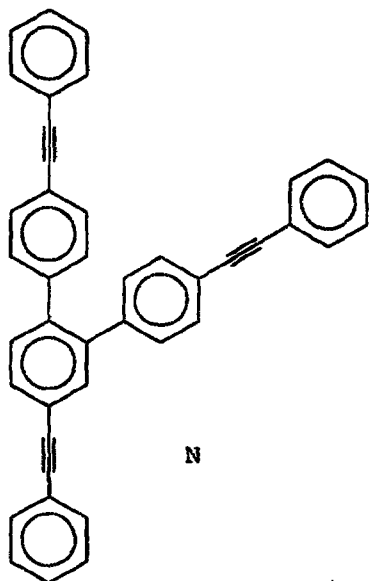
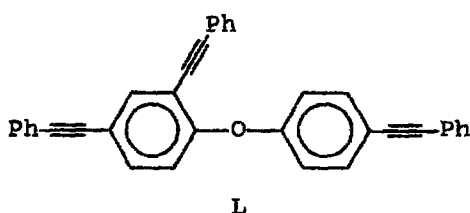


Table I (continued)



Since the compound preparation procedures described above employ standard chemistry practices and it is known that slightly different reactants can require slightly different reaction parameters from those for other reactants, it is to be understood that minor modifications to the reaction parameters set forth such as the use of an excess of one reactant, the use of a catalyst, the use of temperatures slightly higher or lower than room temperature, for example, and/or high speed mixing and other such conventional changes are within the scope of the present invention.

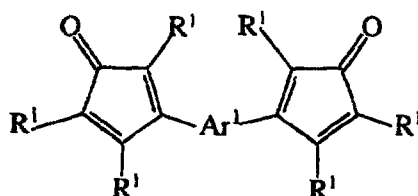
**CLAIMS:**

1. An oligomer, uncured polymer or cured polymer comprising the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups wherein at least some of the polyfunctional compounds contain three or more reactive groups.

2. The oligomer, uncured polymer or cured polymer of Claim 1 wherein the polyfunctional compounds containing the cyclopentadienone groups contain two cyclopentadienone groups and at least some of the polyfunctional compounds containing aromatic acetylene groups contain three or more acetylene groups.

3. The oligomer, uncured polymer or cured polymer of Claim 2 comprising the reaction product of:

(a) a biscyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:

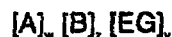


(c) and, optionally, a diacetylene of the formula:



wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹, Ar² and Ar³ are independently an unsubstituted aromatic moiety, or inertly-substituted aromatic moiety, and y is an integer of three or more.

4. The oligomer or uncured polymer having the formula:

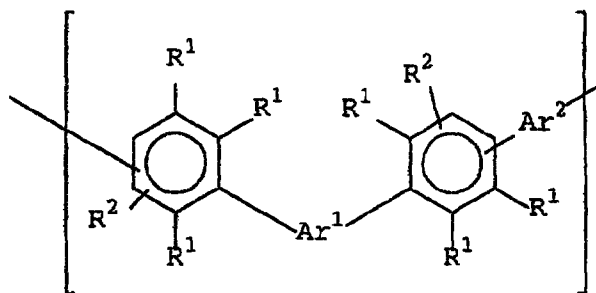


wherein A has the structure:

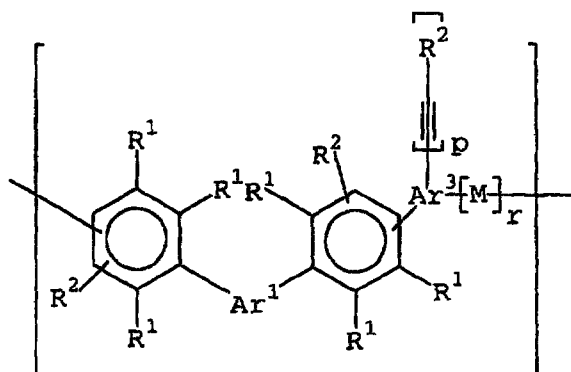
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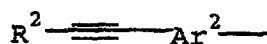
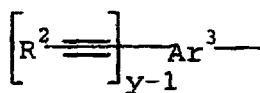
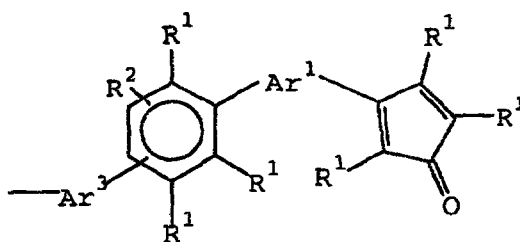
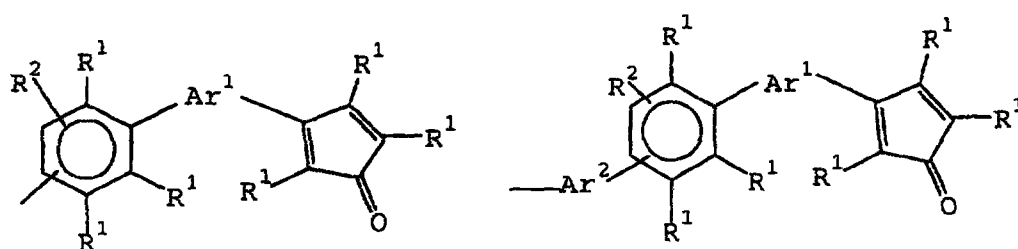


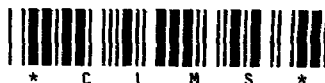
and B has the structure:



endgroups EG are independently represented by any one of the formulas:

EG=





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wherein R^1 and R^2 are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar^1 , Ar^2 and Ar^3 are independently an unsubstituted aromatic moiety or inertly-substituted aromatic moiety and M is a bond, y is an integer of three or more, p is the number of unreacted acetylene groups in the given mer unit, r is one less than the number of reacted
5 acetylene groups in the given mer unit and $p+r=y-1$, z is an integer from 0 to 1000; w is an integer from 0 to 1000 and v is an integer of two or more.

5. The oligomer, uncured polymer or cured polymer of Claim 3 formed by the reaction of:

- (a) Compounds K and G;
- 10 (b) Compounds K, H and G;
- (c) Compounds K, H and L;
- (d) Compounds K, H and Q;
- (e) Compounds K and N;
- (f) Compounds K, O and G;
- 15 (g) Compounds K, P and G;
- (h) Compounds K, O and L;
- (i) Compounds K, P and L;
- (j) Compounds K, O and Q;
- (k) Compounds K, P and Q;
- 20 (l) Compounds K and L; or
- (m) Compounds K and Q,

wherein Compound G is 1,3,5-tris(phenylethynyl)benzene; Compound H is 4,4'-bis(phenylethynyl)diphenyl ether; Compound K is 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone); Compound L is 2,4,4'-tris(phenylethynyl)diphenyl ether;
25 Compound N is 4,4',4''-tris(phenylethynyl)-o-terphenyl; Compound O is 1,3-bis(phenylethynyl)benzene; Compound P is 1,4-bis(phenylethynyl)benzene and Compound Q is 1,2,4-tris(phenylethynyl)benzene.

6. An uncured or cured polymer formed by heating the oligomer or uncured polymer of Claim 3, 4 or 5 at a temperature and for a time to react a sufficient number of the
30 pendant and terminal acetylene groups to achieve gelation.

7. The oligomer, uncured polymer or cured polymer of Claim 3 formed from the reaction of 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone), 1,3,5-tris(phenylethynyl)benzene and 4,4'-bis(phenylethynyl) diphenyl ether.

8. The oligomer, uncured polymer or cured polymer of Claim 3 formed from
35 the reaction of 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopentadienone) and 1,3,5-tris(phenylethynyl)benzene.

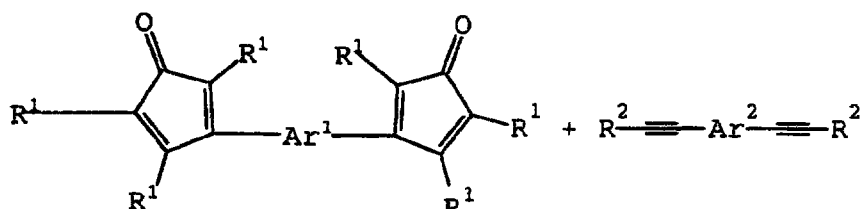


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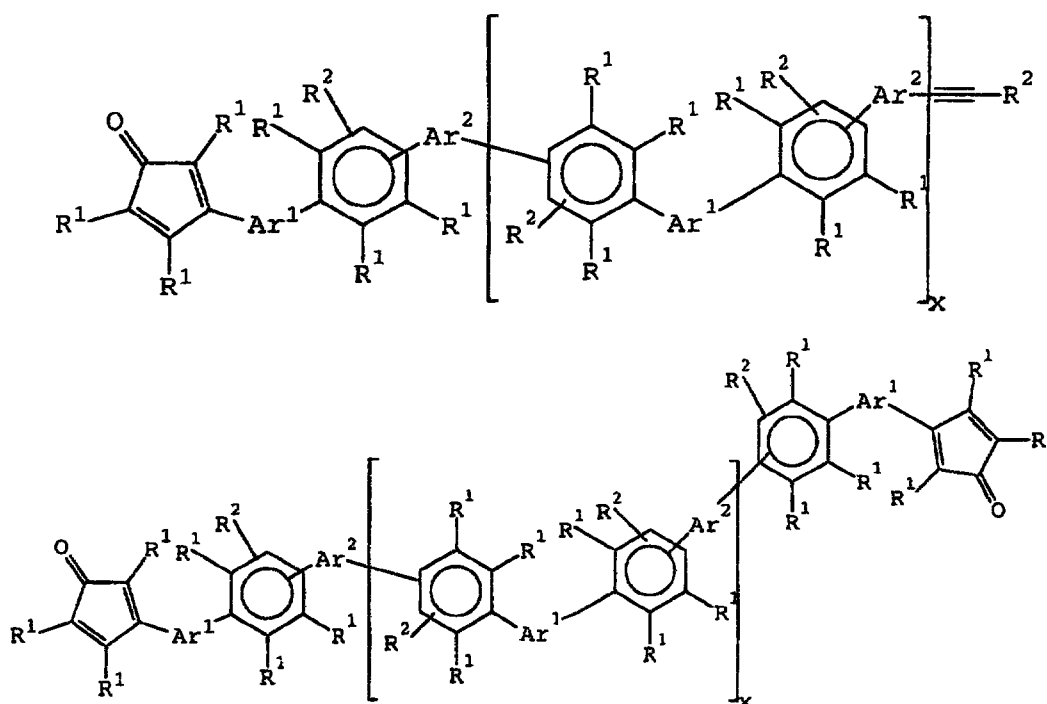
9. An oligomer comprising the reaction product of aromatic cyclopentadienone groups of one or more polyfunctional compounds with the aromatic acetylene groups of the same or a different polyfunctional compound, wherein the oligomer fills a gap that is one micrometer deep and one half micrometer across without leaving a void when cured.

5 10. The oligomer of Claim 9 wherein the polyfunctional compounds are a biscyclopentadienone and a diacetylene of the general formulas:



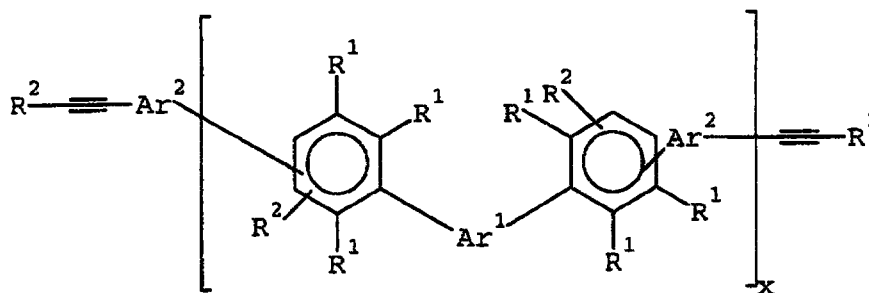
10 wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹ and Ar² are independently an unsubstituted or inertly-substituted aromatic moiety.

11. The oligomer of Claim 9 wherein the oligomers have one or more of the following formulas:



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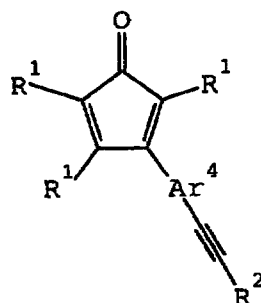
wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹ and Ar² are independently an unsubstituted or inertly-substituted aromatic moiety and x is an integer from 1 to 50.

- 5 12. The oligomer of Claim 9 wherein the oligomer is the reaction product of:
- (1) Compounds K and H;
 - (2) Compounds K and O;
 - (3) Compounds K and P;

10 wherein Compound H is 4,4'-bis(phenylethynyl)-diphenyl ether; Compound K is 3,3'-(oxydi-1,4-phenylene)-bis(2,4,5-triphenylcyclopentadienone); Compound O is 1,3-bis(phenylethynyl)benzene and Compound P is 1,4-bis(phenylethynyl)benzene.

13. The oligomer of Claim 12 wherein the oligomer has a number average molecular weight of from 1000 to 15,000 as determined by size exclusion chromatography using polystyrene calibration standards.

- 15 14. A polyfunctional compound of the general formula:



wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar⁴ is an unsubstituted or inertly-substituted aromatic moiety.

- 20 15. Oligomers, uncured polymers and cured polymers comprising the reaction product of the polyfunctional compound of Claim 14.

16. Oligomers, uncured polymers and cured polymers comprising the reaction product of at least one aromatic monomer containing at least one cyclopentadienone moiety and at least one acetylene moiety.



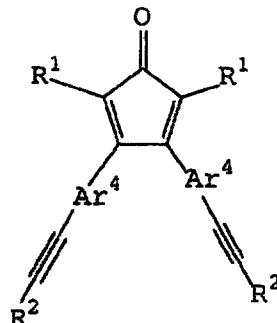


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17. The oligomer, uncured polymer or cured polymer of Claim 16 formed by the reaction of 4-(4-(phenylethynyl)phenyl)-2,3,5-triphenylcyclopentadienone or 4-(4-ethynylphenyl)-2,3,5-triphenyl-cyclopentadienone.

18. A polyfunctional compound of the general formula:



wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and each Ar⁴ is independently an unsubstituted aromatic moiety or inertly-substituted aromatic moiety.

19. An oligomer, uncured polymer or cured polymer formed by the reaction of the compound of Claim 18.

20. The oligomer, uncured polymer or cured polymer of Claim 19 formed by the reaction of 3,4-bis(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone or 3,4-bis(3-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone.

21. A process comprising applying the oligomer or uncured polymer of Claim 1, 3, 4, 8 or 10 to a surface and heating to react additional cyclopentadienone or acetylene moieties to form an uncured polymer or a cured polymer.

22. An integrated circuit article comprising an active substrate containing transistors and an electrical interconnect structure containing patterned metal lines separated, at least partially, by layers or regions of the dielectric material comprising the oligomer, uncured polymer or cured polymer of Claim 1, 3, 4, 8, 10 or 16.

23. 4-(4-(Phenylethynyl)phenyl)-2,3,5-triphenylcyclopentadienone.

24. 4-(4-Ethynylphenyl)-2,3,5-triphenylcyclopentadienone.

25. 3,4-Bis(4-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone or 3,4-Bis-(3-(phenylethynyl)phenyl)-2,5-diphenylcyclopentadienone.

26. 4,4"-Bis(phenylethynyl)-o-terphenyl or 2,4,4'-tris(phenylethynyl)diphenyl ether or 4,4',4"-tris(phenylethynyl)-o-terphenyl.

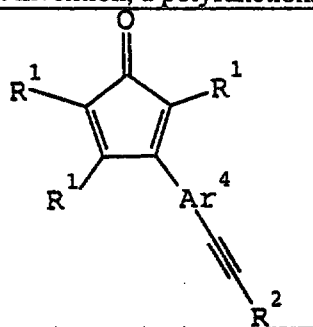
27. 3,3'-(1,4-Phenylene)bis(2,5-di-(4-fluorophenyl)-4-phenylcyclopentadienone).

A feature of the invention is that it comprises the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups wherein at least some of the polyfunctional compounds contain three or more reactive groups. An advantage of such a reaction product is that it may gap fill and planarize patterned surfaces, and as cured have high thermal stability, a high glass transition temperature and a low dielectric constant.

In a second, preferred aspect, the present invention is an oligomer, uncured polymer or cured polymer comprising the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and one or more polyfunctional compounds containing two or more aromatic acetylene groups, wherein at least some of the polyfunctional compounds containing aromatic acetylene groups contain three or more acetylene groups.

A feature of the second aspect of the invention is that it comprises the reaction product of at least one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups, wherein at least some of the polyfunctional compounds containing aromatic acetylene groups contain three or more acetylene groups. An advantage of such a reaction product is that it may gap fill and planarize patterned surfaces, and as cured have high thermal stability, a high glass transition temperature and a low dielectric constant.

In a third preferred aspect of the present invention, a polyfunctional compound of the general formula:



R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar⁴ is an unsubstituted or inertly-substituted aromatic moiety.

In a fourth preferred aspect of the present invention, the oligomers, uncured polymers and cured polymers comprising the reaction product of the polyfunctional compound of the third aspect mentioned above.

In a fifth preferred aspect of the present invention, the oligomers, uncured polymers and cured polymers comprising the reaction product of at least one aromatic monomer containing at least one cyclopentadienone moiety and at least one acetylene moiety.

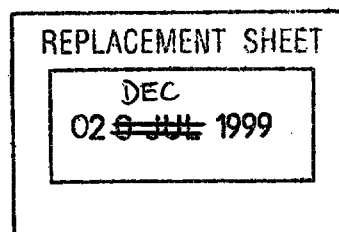
High thermal stability, a high glass transition temperature, a low dielectric constant and the ability to gap fill and planarize patterned surfaces make the compositions of the invention suitable as polymer dielectrics in microelectronics fabrication. In particular, the combination of low dielectric constant, high thermal stability and high glass transition temperature permit the use of the compositions of the invention as interlayer dielectrics in integrated circuits.

Preferably, the oligomers and polymers and corresponding starting monomers of the present invention are:

I. Oligomers and polymers of the general formula:



wherein A has the structure:



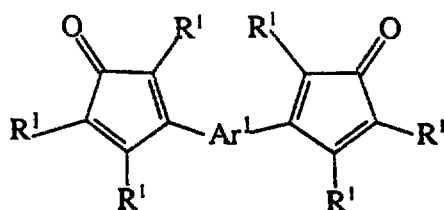
CLAIMS:

1. An oligomer, uncured polymer or cured polymer comprising the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups wherein at least some of the polyfunctional compounds contain three or more reactive cyclopentadienone or acetylene groups.

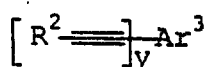
2. The oligomer, uncured polymer or cured polymer of Claim 1 wherein the polyfunctional compounds containing the cyclopentadienone groups contain two cyclopentadienone groups and at least some of the polyfunctional compounds containing aromatic acetylene groups contain three or more acetylene groups.

3. The oligomer, uncured polymer or cured polymer of Claim 2 comprising the reaction product of:

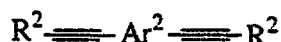
(a) a biscyclopentadienone of the formula:



(b) a polyfunctional acetylene of the formula:

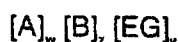


(c) and, optionally, a diacetylene of the formula:



wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹, Ar² and Ar³ are independently an unsubstituted aromatic moiety, or inertly-substituted aromatic moiety, and y is an integer of three or more.

4. The oligomer or uncured polymer having the formula:



wherein A has the structure:

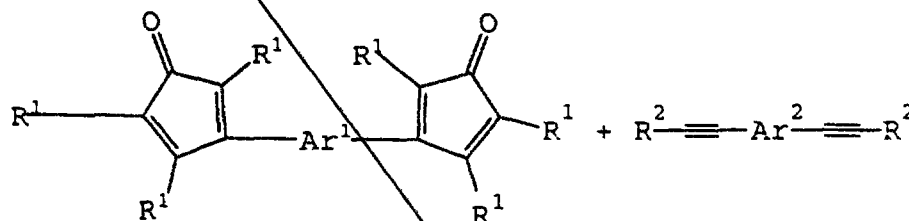


~~9. An oligomer comprising the reaction product of aromatic cyclopentadienone~~

groups of one or more polyfunctional compounds with the aromatic acetylene groups of the same or a different polyfunctional compound, wherein the oligomer fills a gap that is one micrometer deep and one half micrometer across without leaving a void when cured.

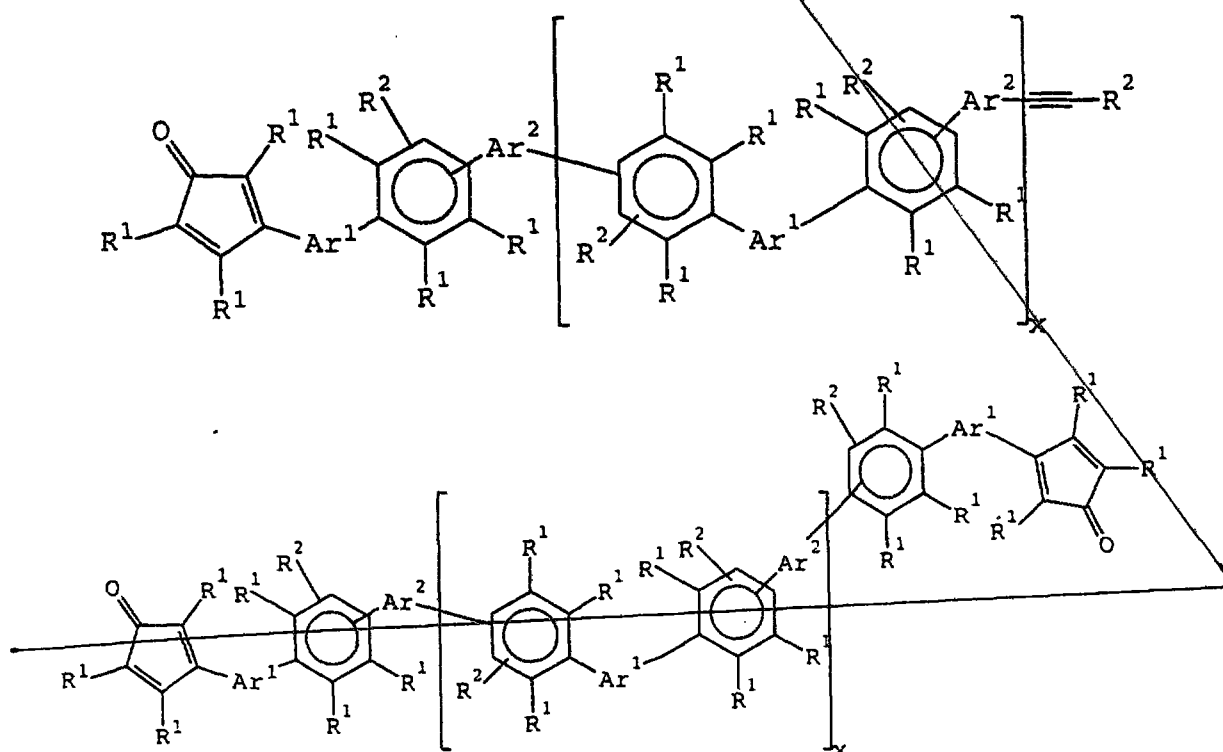
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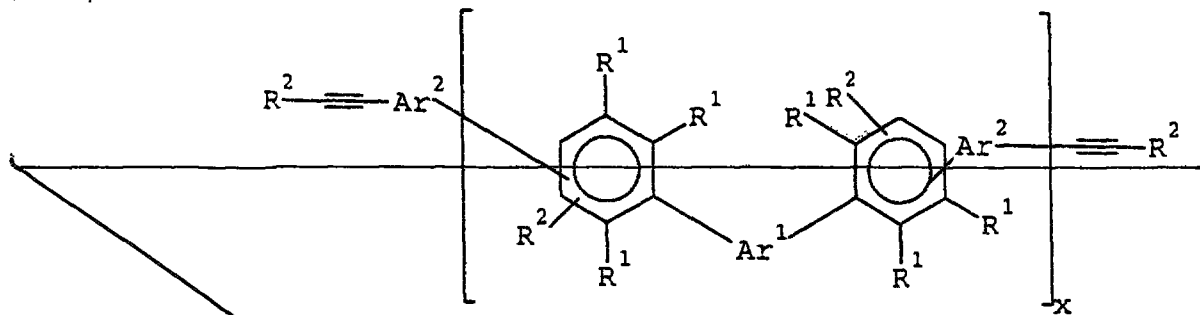
10. The oligomer of Claim 9 wherein the polyfunctional compounds are a biscyclopentadienone and a diacetylene of the general formulas:



wherein R¹ and R² are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar¹ and Ar² are independently an unsubstituted or inertly-substituted aromatic moiety.

11. The oligomer of Claim 9 wherein the oligomers have one or more of the following formulas:





wherein R^1 and R^2 are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar^1 and Ar^2 are independently an unsubstituted or inertly-substituted aromatic moiety and x is an integer from 1 to 50.

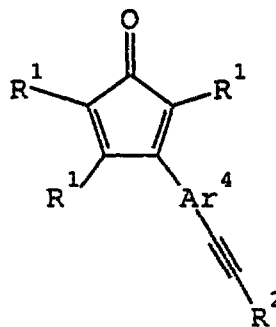
5 12. The oligomer of Claim 9 wherein the oligomer is the reaction product of:

- (1) Compounds K and H;
- (2) Compounds K and O;
- (3) Compounds K and P;

10 wherein Compound H is 4,4'-bis(phenylethynyl)-diphenyl ether; Compound K is 3,3'-(oxydi-1,4-phenylene)-bis(2,4,5-triphenylcyclopentadienone); Compound O is 1,3-bis(phenylethynyl)benzene and Compound P is 1,4-bis(phenylethynyl)benzene.

13. The oligomer of Claim 12 wherein the oligomer has a number average molecular weight of from 1000 to 15,000 as determined by size exclusion chromatography using polystyrene calibration standards.

15 14. A polyfunctional compound of the general formula:



wherein R^1 and R^2 are independently H or an unsubstituted or inertly-substituted aromatic moiety and Ar^4 is an unsubstituted or inertly-substituted aromatic moiety.

20 15. Oligomers, uncured polymers and cured polymers comprising the reaction product of the polyfunctional compound of Claim 14.

16. Oligomers, uncured polymers and cured polymers comprising the reaction product of at least one aromatic monomer containing at least one cyclopentadienone moiety and at least one acetylene moiety.



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(21) International Application Number: PCT/US97/15142 (22) International Filing Date: 28 August 1997 (28.08.97) (30) Priority Data: 08/711,838 10 September 1996 (10.09.96) US 08/834,677 1 April 1997 (01.04.97) US (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Midland, MI 48674 (US). (72) Inventors: GODSCHALX, James, P.; 2205 Plymouth Street, Midland, MI 48642 (US); ROMER, Duane, R.; 4025 Lowell Court, Midland, MI 48642 (US); SO, Ying, Hung; 1524 Dilloway Drive, Midland, MI 48640 (US); LYSENKO, Zenon; 214 West Meadowbrook Drive, Midland, MI 48640 (US); MILLS, Michael, E.; 1604 Avalon Street, Midland, MI 48642 (US); BUSKE, Gary, R.; 613 Sylvan Lane, Midland, MI 48640 (US); TOWNSEND, Paul, H., III; 1102 Willard Street, Midland, MI 48642 (US); SMITH, Dennis, W., Jr.; 4607 Pleasant Trail, Fresno, TX 77545 (US). MARTIN, Steven, J.; 3019 Scarborough Lane, Midland, MI 48640 (US); DEVRIES, Robert, A.; 2408 Greenbrier Terrace, Midland, MI 48642 (US).		(74) Agent: DAMOCLES, Nemia, C.; Patent Dept., P.O. Box 1967, Midland, MI 48641-1967 (US). (81) Designated States: IL, JP, KR, NO, SO, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report.
(54) Title: POLYPHENYLENE OLIGOMERS AND POLYMERS (57) Abstract An oligomer, uncured polymer or cured polymer comprising the reaction product of one or more polyfunctional compounds containing two or more cyclopentadienone groups and at least one polyfunctional compound containing two or more aromatic acetylene groups wherein at least some of the polyfunctional compounds contain three or more reactive groups. Such oligomers and uncured polymers may be cured to form cured polymers which are useful as dielectrics in the microelectronics industry, especially for dielectrics in integrated circuits.		