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(54) **Title:** MODIFIED POLYCYCLIC POLYMERS

(57) **Abstract**

The present invention relates to cyclic polymers and their use in photolithographic applications. The cyclic polymers contain a pendant acid labile functional group and a functional group containing a protected hydroxyl moiety. The polymers are post modified by deprotecting the pendant hydroxyl moiety and reacting the deprotected hydroxyl containing moiety with a coreactant. The post-functionalized polymers find application in chemically amplified photoresist compositions.

MODIFIED POLYCYCLIC POLYMERS

BACKGROUND OF THE INVENTION

1. Technical Field

The present invention relates to polycyclic polymers and methods for their use in photolithographic applications. More specifically, the invention is related to the modification of polycyclic polymers containing pendant functional groups and to their uses in photoresist compositions for the manufacture of integrated circuits (IC's).

2. Background

Trends in the electronics industry continually require IC's that are faster, and consume less power. To meet these specifications the IC must be of a high density having sub-micron feature dimensions. Conducting lines must be made thinner and placed closer together. Reducing the spacing between conductive lines results in a concomitant increase in the efficiency of the IC enabling a greater storage capacity and faster processing of information on a computer chip. To achieve thinner line widths and smaller feature sizes higher patterning resolution is necessary.

The patterning of IC's is carried out according to various lithography techniques known in the art. Photolithography employing ultraviolet (UV) light and increasingly deep UV light or other radiation is a fundamental and important technology utilized in the production of IC devices. A photosensitive polymer film (photoresist) is applied over a substrate surface (e.g., wafer) and dried. A photomask containing the desired patterning information is then placed in close proximity to the photoresist film. The photoresist is irradiated through the overlying photomask by one of several types of imaging radiation including UV light, electron beams, x-rays, or ion beams. Upon exposure to radiation, the photoresist undergoes a chemical change with attendant changes in solubility. After irradiation, the substrate is soaked in a solution that develops (i.e., selectively removes either the exposed or unexposed regions) the patterned selectively removes either the exposed or unexposed regions) the patterned images in the photosensitive polymer film. Depending on the type of photoresist used, or the polarity of the developing solvent, either the exposed or nonexposed areas of film are removed in the developing process to expose the underlying substrate, after which the patterned exposed or unwanted substrate material is removed or changed by an etching process leaving the desired pattern in a functional layer of the wafer. The remaining photoresist material functions as a protective barrier against the etching process. Removal of the remaining photoresist material gives the patterned circuit. Etching is accomplished by plasma etching, sputter etching, and reactive ion etching (RIE).

Etching generally involves passing a gas through a chamber and ionizing the gas by applying a potential across two electrodes in the presence of the gas. The plasma containing the ionic species generated by the potential is used to etch a substrate placed in the chamber. The ionic species generated in the plasma are directed to the patterned substrate where they interact with the surface material forming volatile products that are removed from the surface. Reactive ion etching provides well defined vertical sidewall profiles in the substrate as well as substrate to substrate etching uniformity. Because of these advantages, the reactive ion etching technique has become the standard in IC manufacture.

In the manufacture of high density IC's the coating, exposure, and development of the photoresist film is critical. It is important to control the line width of the imaged and developed photoresist to close tolerances. The profiles of the patterned photoresist structures must be straight with vertical sidewalls. In addition, the patterned resist must be tolerant to subsequent IC processing steps such as RIE. These high performance polymer resists require superior tuning of several polymer properties such as hydrophilicity, adhesion, differential solubilities between the radiation exposed and unexposed regions (e.g., good resolution and contrast capabilities) and RIE resistance. Accordingly, chemically amplified resist compositions are becoming favored in the manufacture of these high density IC devices.

U.S. Patent 4,491,628 to Ito et al. discloses a chemically amplified photoresist composition containing a photosensitive acid generator and a polymeric component having pendant acid labile groups including t-butyl esters of carboxylic acids and t-butyl carbonates of phenols.

U.S. Patent 5,372,912 to Allen et al. discloses a chemically amplified photoresist composition comprising an acrylate based copolymer, a phenolic binder and a photosensitive acid generator. The copolymer component comprises the reaction product of acrylic or methacrylic acid, alkyl acrylates or methacrylates, and a monomer having a pendant acid labile group such as t-butyl esters of carboxylic and t-butyl carbonates of phenols. The properties of the copolymer can be tailored by varying the content of the disclosed monomers.

International Patent Application Publication WO 97/33198 to The B.F.Goodrich Company discloses a chemically amplified photoresist composition comprising a polycyclic polymer containing repeating units having pendant acid labile groups. Additionally, the polymer may contain polycyclic repeating units having a variety of pendant neutral groups, acid groups, alkyl groups, and mixtures thereof. These polycyclic polymers have exhibited good transparency to short wave length imaging radiation while being resistant to RIE processing techniques. In addition, the wide variety of applicable functional groups enable the artisan to tailor the properties of the polymer to a wide range of specifications. The acid labile groups on the polymer are cleaved to confer polarity or solubility to the polymer, while the neutral groups function to impart hydrophilicity, solubility, promote wetting, and improve film properties. The pendant acid group contributes to the hydrophilicity/wetting of the polymer as well as conferring adhesive characteristics thereto. Pendant alkyl substituents are useful to vary the Tg of the polymer system.

While the foregoing polycyclic polymers exhibit flexibility in property tailoring for high performance photoresist applications through the use of selected pendant functional groups, a drawback exists in that cycloolefinic monomers containing certain of these functionalities are difficult to efficiently polymerize directly. For example, hydroxyl (e.g., alcohols, carboxylic acids, phenols) and nitrogen (e.g., amides, nitriles) containing functionalities may inhibit the catalyst system utilized to polymerize these functional cycloolefin monomers, resulting in reduced yields of the desired polymer. In addition, cycloolefin monomers with certain functional groups may be difficult to synthesize and purify via conventional synthesis routes or might not always be commercially available. Accordingly, there is a need for alternate synthesis routes for photoresist polymers having pendant functional groups that are technically feasible, efficient, and economical.

SUMMARY OF THE INVENTION

It is a general object of the invention to provide alternate methods for functionalizing polymers useful in photoresist compositions.

It is a further object of the invention to post-functionalize polymers comprising polycyclic repeating units.

It is still a further object of the invention to post-functionalize a polycyclic polymer comprising repeating units containing pendant acid labile moieties.

It is another object of the invention to provide alternate methods of functionalizing polycyclic polymers with hydroxyl, nitrogen and sulfur containing groups.

It is still another object of the invention to introduce carboxylic acid containing moieties into a polycyclic polymer backbone through a post-functionalization reaction.

It is another object of the invention to provide photoresist polymers with increased hydrophilicity.

It has been found that the above described objects of the present invention are accomplished by a method for preparing a polycyclic polymer suitable for use in photoresist compositions by introducing difficult to polymerize functionalities into the polymer via a post-functionalization process, said process comprising: (a) providing a polycyclic base polymer composition comprising repeating units containing pendant acid labile groups and repeating units containing pendant protected hydroxyl containing moieties; (b) deprotecting the hydroxyl containing moieties to give a free hydroxyl group; and (c) reacting the free hydroxyl group with a coreactive moiety to give a post-functionalized moiety.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a SEM micrograph of a printed image on a 50/50 oxalate/t-butyl ester resist polymer at 0.30 micron feature resolution.

FIG. 2 is a SEM micrograph of a printed image on a resist polymer of the invention containing 10 mole percent of repeating units having pendant carboxylic acid functionality at 0.30 micron feature resolution.

FIG. 3 is a SEM micrograph of a printed image on a resist polymer of the invention containing 10 mole percent of repeating units having pendant carboxylic acid functionality at 0.15 micron feature resolution and a 1:1 pitch.

FIG. 4 is a SEM micrograph of a printed image on a resist polymer of the invention containing 10 mole percent of repeating units having pendant carboxylic acid functionality at 0.12 micron feature resolution and a 2:1 pitch.

FIG. 5 is a SEM micrograph of a printed image on a resist polymer of the invention containing 20 mole percent of repeating units having pendant carboxylic acid functionality at 0.16 micron feature resolution and a 1:1 pitch.

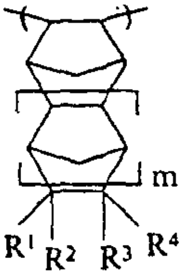
FIG 6 is a SEM micrograph of a printed image on a resist polymer of the invention containing 20 mole percent of repeating units having pendant carboxylic acid functionality at 0.10 micron feature resolution and a 3:1 pitch.

DETAILED DESCRIPTION

This invention is directed to a process for the direct incorporation of functional groups into a base polymer comprising polycyclic repeating units containing pendant acid labile groups and polycyclic repeating units containing a pendant moiety having a protected hydroxyl group. The post-functionalized polymers find application in chemically amplified photoresist compositions. The process of the present invention useful in situations where the desired functional group can not be incorporated into the polymer by the direct polymerization of monomers containing the desired functionality.

In one aspect of the invention a base polymer comprising polycyclic repeating units set forth under Formulae **I** and **II** described below is post-functionalized to give a polymer suitable for chemically amplified photoresist applications. The repeating units of Formula I contain a pendant acid labile group and the repeating units set forth under Formula **II** contain a pendant protected hydroxyl containing moiety. In addition, the base polymer composition can optionally contain polycyclic repeating units described under Formula **III** below. The base polymer of the invention is post-functionalized through the pendant protected hydroxyl containing moiety.

The acid labile containing repeating units of the invention are represented by Formula **I** below.



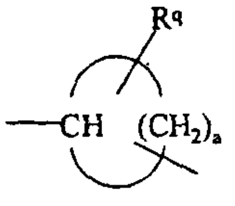
I

wherein R^1 to R^4 independently represent a substituent selected from the group $-(A)_nC(O)OR^*$, $-(A)_n-C(O)OR$, $-(A)_n-OR$, $-(A)_n-OC(O)R$, $-(A)_n-C(O)R$, $-(A)_n-OC(O)OR$, $-(A)_n-OCH_2C(O)OR^*$, $-(A)_n-C(O)O-A'-OCH_2C(O)OR^*$,

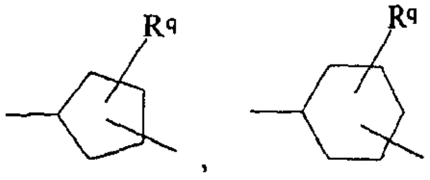
$-(A)_n-OC(O)-A'-C(O)OR^*$, $-(A)_n-C(R)_2CH(R)(C(O)OR^{**})$, and $-(A)_n-C(R)_2CH(C(O)OR^{**})_2$ subject to the proviso that at least one of R^1 to R^4 is selected from an acid labile group containing R^*, preferably, $-(A)_nC(O)OR^*$.

A and A′ independently represent a divalent bridging or spacer radical selected from divalent hydrocarbon radicals, divalent cyclic hydrocarbon radicals, divalent oxygen containing radicals, and divalent cyclic ethers and cyclic diethers, m is an interger from 0 to 10, preferably, 0 or 1; and n is an integer of 0 or 1. When n is 0 it should be apparent that A represents a single covalent bond. By divalent is meant that a free valence at each terminal end of the radical are attached to two distinct groups. The divalent hydrocarbon radicals can be represented by the formula $-(C_dH_{2d})-$ where d represents the number of carbon atoms in the alkylene chain and is an integer from 1 to 10. The divalent hydrocarbon radicals are preferably selected from linear and branched (C_1 to C_{10}) alkylene such as methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, and decylene. When branched alkylene radicals are contemplated, it is to be understood that a hydrogen atom in the linear alkylene chain is replaced with a linear or branched (C_1 to C_5) alkyl group.

The divalent cyclic hydrocarbon radicals include substituted and unsubstituted (C_3 to C_8) cycloaliphatic moieties represented by the formula:

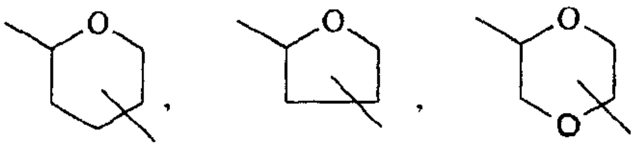


wherein a is an integer from 2 to 7 and R^q when present represents linear and branched (C_1 to C_{10}) alkyl groups. Preferred divalent cycloalkylene radicals include cyclopentylene and cyclohexylene moieties represented by the following structures:



wherein R^q is defined above. As illustrated here and throughout this specification, it is to be understood that the two bond lines projecting from the cyclic structures and/or formulae represent the divalent nature of the moiety and indicate the points at which the carbocyclic atoms are bonded to the adjacent molecular moieties defined in the respective formulae. As is conventional in the art, the diagonal bond line projecting from the center of the cyclic structure indicates that the bond is optionally connected to any one of the carbocyclic atoms in the ring. It is also to be understood that the carbocyclic atom to which the bond line is connected will accommodate one less hydrogen atom to satisfy the valence requirement of carbon.

Preferred divalent cyclic ethers and diethers are represented by the structures:



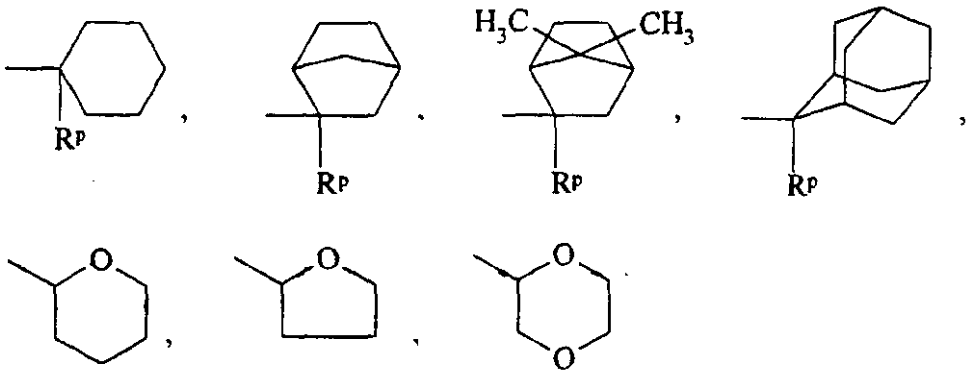
The divalent oxygen containing radicals include $(C_2$ to $C_{10})$ alkylene ethers and polyethers. By $(C_2$ to $C_{10})$ alkylene ether is meant that the total number of carbon atoms in the divalent ether moiety must at least be 2 and can not exceed 10. The divalent alkylene ethers are represented by the formula -alkylene-O-alkylene- wherein each of the alkylene groups that are bonded to the oxygen atom can be the same or different and are selected from methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, and nonylene. The simplest divalent alkylene ether of the series is the radical

$-CH_2-O-CH_2-$. Preferred polyether moieties include divalent radicals of the formula:

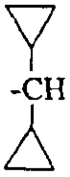
$$-\!\left(CH_2(CH_2)_xO\right)_y\!-$$

wherein x is an integer from 1 to 5 and y is an integer from 2 to 50 with the proviso that the terminal oxygen atom on the polyether spacer moiety can not be directly linked to a terminal oxygen atom on an adjacent group to form a peroxide linkage. In other words, peroxide linkages (i.e., -O-O-) are not contemplated when polyether spacers are linked to any of the terminal oxygen containing substituent groups set forth under R^1 to R^4 above.

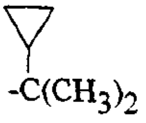
In the above formulae R represents linear and branched (C_1 to C_{10}) alkyl. R* represents moieties (i.e., acid labile, blocking or protecting groups) that are cleavable by photoacid initiators selected from $-C(CH_3)_3$, $-CH(R^p)OCH_2CH_3$, $-CH(R^p)OC(CH_3)_3$, or the following cyclic groups:



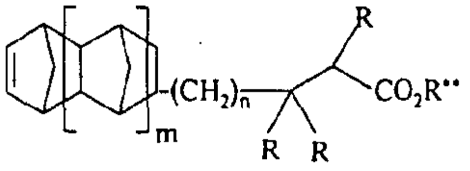
R^p represents hydrogen or a linear or branched (C_1 to C_5) alkyl group. The alkyl substituents include methyl, ethyl, propyl, i-propyl, butyl, i-butyl, t-butyl, pentyl, t-pentyl and neopentyl. In the above structures, the single bond line projecting from the cyclic groups indicates the carbon atom ring position where the protecting group is bonded to the respective substituent. Examples of acid labile groups include 1-methyl-1-cyclohexyl, isobornyl, 2-methyl-2-isobornyl, 2-methyl-2-adamantyl, tetrahydrofuranyl, tetrahydropyranyl, 3-oxocyclohexanonyl, mevalonic lactonyl, 1-ethoxyethyl, 1-t-butoxy ethyl, dicyclopropylmethyl (Dcpm), and dimethylcyclopropylmethyl (Dmcp) groups. R** independently represents R and R* as defined above. The Dcpm and Dmcp groups are respectively represented by the following structures:

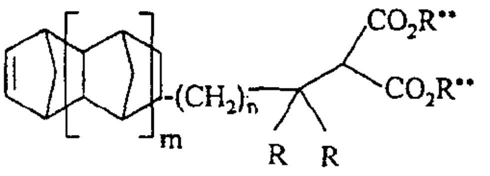


, and



Polycyclic monomers of the above formula with a substituent selected from the group $-(CH_2)_nC(R)_2CH(R)(C(O)OR^{**})$ or $-(CH_2)_nC(R)_2CH(C(O)OR^{**})_2$ can be represented as follows:



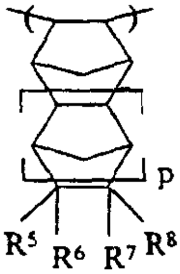


wherein m is as defined above and n is an integer from 0 to 10.

It should be apparent to those skilled in the art that any photoacid cleavable moiety is suitable in the practice of the invention so long as the polymerization reaction is not substantially inhibited by same.

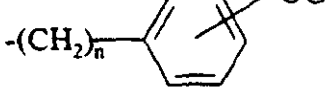
The preferred acid labile group is a protected organic ester group in which the protecting or blocking group undergoes a cleavage reaction in the presence of an acid. Tertiary butyl esters of carboxylic acids are especially preferred.

The repeating units set forth under Formula **II** below contain a pendant group containing a protected hydroxyl moiety. By hydroxyl moiety is meant any functionality that contains a hydroxyl group. For brevity the protected moiety can also be referred to as a protected-oxy group. The term protected-oxy refers to an oxygen atom that has been protected from undesired reactions. Representative hydroxyl containing functionalities include, for example, alcohols, carboxylic acids, and phenols. By protected hydroxyl moiety means the hydrogen atom on the oxygen atom in the hydroxyl moiety is temporarily replaced by a protecting group. The protecting group serves to protect the functional group from undesired side reactions or to block its undesired reaction with other functional groups or with the catalysts used to polymerize the base polymer. Repeating units containing pendant protected hydroxyl moieties are represented as follows:



II

wherein R^5 to R^8 independently represent hydrogen, linear and branched (C_1 to C_{20}) alkyl, $-(CH_2)_nC(O)OR$, $-(CH_2)_nOR$, $-(CH_2)_nOC(O)R$, $-(CH_2)_nC(O)R$, $-(CH_2)_nOC(O)OR$, wherein R is linear or branched (C_1 to C_{10}) alkyl. At least one of R^5 to R^8 is selected from a protected group represented by $-(CH_2)_nOG$, $-(CH_2)_nC(O)OG$, and $-(CH_2)_n-(C_6$ to $C_{14})$aryl-OG. Representative aryl groups are phenyl, naphthyl, and anthracenyl. When the aryl group is phenyl the hyroxyl protected substituents can be represented as follows:



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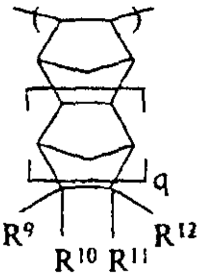
wherein n is an integer from 0 to 10, preferably, 0 to 5; p is an integer from 0 to 5, preferably 0 or 1; and G is a protecting group selected from a substituent of the formula $-Si(R^{15})_3$ wherein R^{15} independently represents linear and branched (C_1 to C_{10}) alkyl, aryl such as phenyl, aralkyl such as phenyl substituted with linear or branched (C_1 to C_5) alkyl groups. Representative silyl groups include trimethylsilyl, triethylsilyl, triisopropylsilyl, dimethylisopropylsilyl, diethylisopropylsilyl, dimethylhexylsilyl, dimethylphenylsilyl, t-butyldimethylsilyl, t-butyldiphenylsilyl, di-t-butylmethylsilyl, tribenzylsilyl, tri-*p*-xylylsilyl, triphenylsilyl, and diphenylmethylsilyl. Preferred protecting groups include trialkylsilyl with trimethylsilyl being the most preferred.

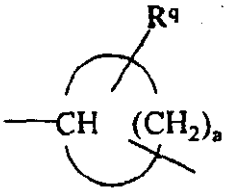
Optionally, the base polymer of the present invention can contain a repeating unit selected from Formula **III** below:



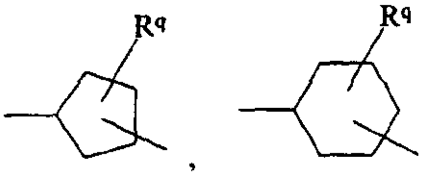
III

wherein R^9 to R^{12} independently represent hydrogen, linear or branched (C_1 to C_{10}) alkyl, or a substituent selected from the group: -(A)$_n$-C(O)OR″, -(A)$_n$-OR″, -(A)$_n$-OC(O)R″, -(A)$_n$-OC(O)OR″, -(A)$_n$-C(O)R″, -(A)$_n$-OC(O)C(O)OR″, -(A)$_n$-O-A′-C(O)OR″, -(A)$_n$-OC(O)-A′-C(O)OR″, -(A)$_n$-C(O)O-A′-C(O)OR″, -(A)$_n$-C(O)-A′-OR″, -(A)$_n$-C(O)O-A′-OC(O)OR″, -(A)$_n$-C(O)O-A′-O-A′-C(O)OR″, -(A)$_n$-C(O)O-A′-OC(O)C(O)OR″, -(A)$_n$-C(R″)$_2$CH(R″)(C(O)OR″), and -(A)$_n$-C(R″)$_2$CH(C(O)OR″)$_2$; and q is an integer from 0 to 5, preferably, 0 or 1. The moieties A and A′ independently represent a divalent bridging or spacer radical selected from divalent hydrocarbon radicals, divalent cyclic hydrocarbon radicals, divalent oxygen containing radicals, and divalent cyclic ethers and cyclic diethers, and n is an integer 0 or 1. When n is 0 it should be apparent that A represents a single covalent bond. By divalent is meant that a free valence at each terminal end of the radical are attached to two distinct groups. The divalent hydrocarbon radicals can be represented by the formula $-(C_dH_{2d})-$ where d represents the number of carbon atoms in the alkylene chain and is an integer from 1 to 10. The divalent hydrocarbon radicals are preferably selected from linear and branched (C_1 to C_{10}) alkylene such as methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, and decylene. When branched alkylene radicals are contemplated, it is to be understood that a hydrogen atom in the linear alkylene chain is replaced with a linear or branched (C_1 to C_5) alkyl group.

The divalent cyclic hydrocarbon radicals include substituted and unsubstituted (C_3 to C_8) cycloaliphatic moieties represented by the formula:

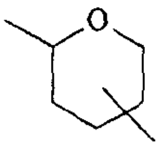


wherein a is an integer from 2 to 7 and R^q when present represents linear and branched (C_1 to C_{10}) alkyl groups. Preferred divalent cycloalkylene radicals include cyclopentylene and cyclohexylene moieties represented by the following structures:



wherein R^q is defined above.

Preferred divalent cyclic ethers and diethers are represented by the structures: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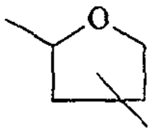
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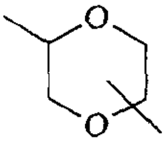
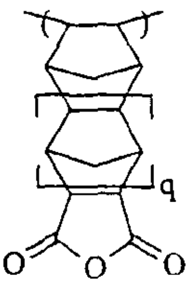


The divalent oxygen containing radicals include (C_2 to C_{10}) alkylene ethers and polyethers. By (C_2 to C_{10}) alkylene ether is meant that the total number of carbon atoms in the divalent ether moiety must at least be 2 and can not exceed 10. The divalent alkylene ethers are represented by the formula -alkylene-O-alkylene- wherein each of the alkylene groups that are bonded to the oxygen atom can be the same or different and are selected from methylene, ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, and nonylene. The simplest divalent alkylene ether of the series is the radical $-CH_2-O-CH_2-$. Preferred polyether moieties include divalent radicals of the formula:

$$-\!\left(CH_2(CH_2)_xO\right)_y\!-$$

wherein x is an integer from 1 to 5 and y is an integer from 2 to 50 with the proviso that the terminal oxygen atom on the polyether spacer moiety can not be directly linked to a terminal oxygen atom on an adjacent group to form a peroxide linkage. In other words, peroxide linkages (i.e., -O-O-) are not contemplated when polyether spacers are linked to any of the terminal oxygen containing substituent groups set forth under R^9 to R^{12} above. R^9 and R^{12} can be taken together with the ring carbon atoms to which they are attached to represent a cyclic anhydride group as shown below:



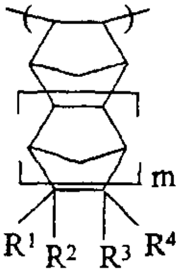
wherein q is defined as above. R″ independently represents, linear and branched (C_1 to C_{10}) alkyl, linear and branched (C_1 to C_{10}) alkoxyalkylene, polyethers, monocyclic and polycyclic (C_4 to C_{20}) cycloaliphatic moieties, cyclic ethers, cyclic ketones, and cyclic esters (lactones). By (C_1 to C_{10}) alkoxyalkylene is meant that a terminal alkyl group is linked through an ether oxygen atom to an alkylene moiety. The radical is a hydrocarbon based ether moiety that can be generically represented as -alkylene-O-alkyl wherein the alkylene and alkyl groups independently contain 1 to 10 carbon atoms each of which can be linear or branched. The polyether radical can be represented by the formula:

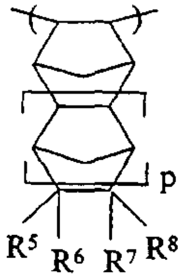
$$-\left(\mathrm{CH_2(CH_2)_xO}\right)_y-\mathrm{R^a}$$

wherein x is an integer from 1 to 5, y is an integer from 2 to 50 and R^a represents or linear and branched (C_1 to C_{10}) alkyl. Preferred polyether radicals include poly(ethylene oxide) and poly(propylene oxide).

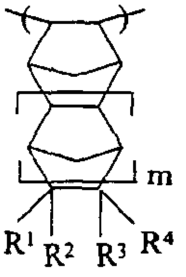
Examples of monocyclic cycloaliphatic monocyclic moieties include cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and the like. Examples of cycloaliphatic polycyclic moieties include, norbornyl, adamantyl, tetrahydrodicyclopentadienyl (tricyclo[5.2.1.0 ^{2,6}] decanyl), and the like. Examples of cyclic ethers include tetrahydrofuranyl and tetrahydropyranyl moieties. An example of a cyclic ketone is a 3-oxocyclohexanonyl moiety.

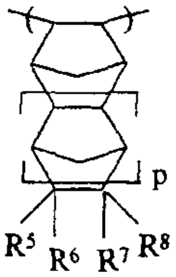
The base polymer according to the present invention comprises repeating units set forth under Formulae **I** and **II** in optional combination with repeating units set forth under Formula **III**. Base polymers comprising repeating units of Formula **I** and Formula **III** are also contemplated within the scope of this invention. Accordingly, the base polymers of the invention comprise the following repeating units:

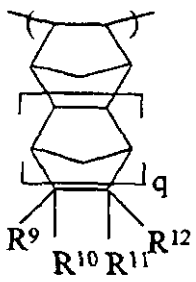




when the optional repeating units described under Formula **III** are included, the base polymers of the invention comprise the following repeating units:





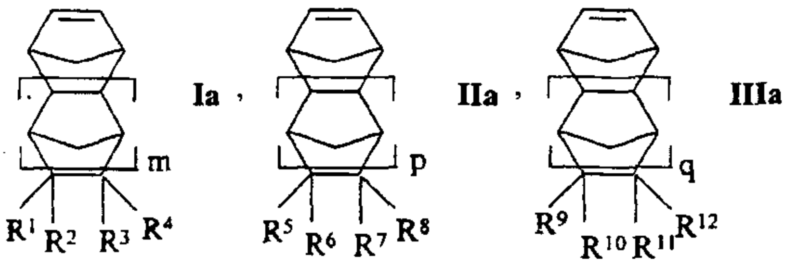


In the above described polymers R^1 to R^{12}, m, p, and q are as previously defined and at least one of R^1 to R^4 must be an acid labile group and at least one of R^5 to R^8 must be a protected hydroxyl containing moiety. The base polymers of the invention can comprise any combination of repeating units so long as pendant protected hydroxyl containing moieties and pendant acid labile groups are present on the polymer.

The base polymers of the present invention generally comprise about 5 to about 95 mole percent of polycyclic repeating units containing the pendant acid labile group, and about 95 to about 5 mole percent of polycyclic repeating units containing the pendant protected hydroxyl moiety. Optionally, the polymers of the invention can contain about 5 to about 50 mole percent of the repeating unit set forth under Formula **III**.

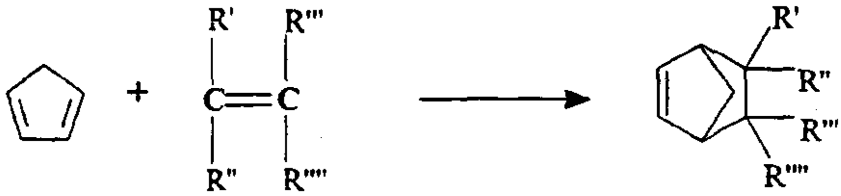
The base polymers of the present invention are preferably addition polymers comprising polycyclic repeating units that are connected to one another via 2,3-linkages that are formed across the double bond contained in the norbornene-type moiety of the prepolymerized polycyclic monomer.

The base polymers of the invention can be polymerized in the presence of a single or multi-component Group VIII transition metal catalyst system from the appropriately functionalized norbornene-type monomers as set forth under Formulae **Ia**, **IIa** and **IIIa** below:

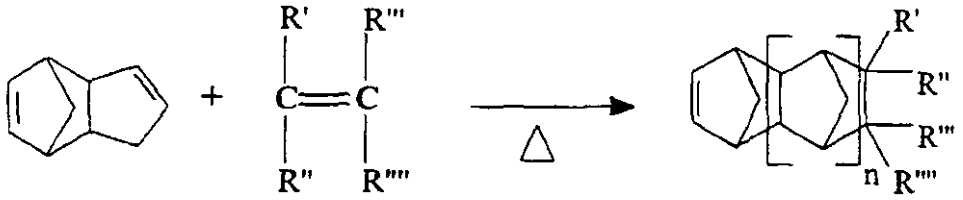


wherein R^1 to R^{12}, m, p, and q have been previously described.

An economical route for the preparation of the substituted polycyclic monomers of the invention relies on the Diels-Alder reaction in which cyclopentadiene (CPD) or substituted CPD is reacted with a suitably substituted dienophile at elevated temperatures to form a substituted polycyclic adduct generally shown by the following reaction scheme:

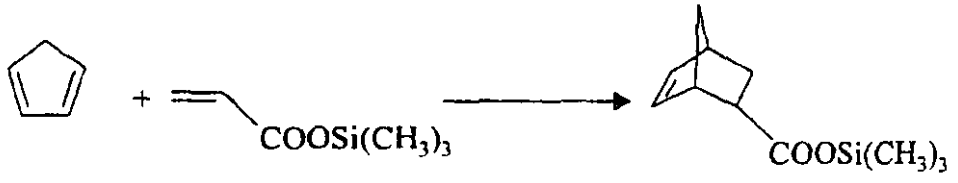


Other polycyclic adducts can be prepared by the thermal pyrolysis of dicyclopentadiene (DCPD) in the presence of a suitable dienophile. The reaction proceeds by the initial pyrolysis of DCPD to CPD followed by the Diels-Alder addition of CPD and the dienophile to give the adducts as shown below:



wherein R′ to R′′′′ independently represents the substituents defined under R^1 to R^{12} in Formulae **I**, **II**, **III**, above.

For example the trimethylsilyl ester of norbornene can be prepared by the Diels-Alder reaction of cyclopentadiene with acryloxytrimethylsilane in accordance with the following reaction scheme:



Catalysts and methods to polymerize these monomers are described in International Patent Application Publication No. WO97/33198 to The BFGoodrich Company, published on June 12, 1997, the entire disclosure of which is hereby incorporated by reference.

A single component catalyst system useful in making polymers utilized in this invention is represented by the formula:

$$E_nNi(C_6F_5)_2$$

wherein n is 1 or 2 and E represents a neutral 2 electron donor ligand. When n is 1, E preferably is a π-arene ligand such as toluene, benzene, and mesitylene.

When n is 2, E is preferably selected from diethylether, tetrahrydrofuran (THF), and dioxane. The ratio of monomer to catalyst in the reaction medium can range from about 5000:1 to about 50:1. The reaction can be run in a hydrocarbon solvent such as cyclohexane, toluene, and the like at a temperature range from about 0°C to about 70°C, preferably 10°C to about 50°C, and more preferably from about 20°C to about 40°C. Preferred catalysts of the above formula are (toluene)bis(perfluorophenyl) nickel, (mesitylene)bis(perfluorophenyl) nickel, (benzene)bis(perfluorophenyl) nickel, bis(tetrahydrofuran)bis(perfluorophenyl) nickel and bis(dioxane)bis(perfluorophenyl) nickel.

An essential feature of the invention is that the hydroxyl containing moiety of the monomer set forth under Formula **IIa** be protected when these monomers are introduced into the polymerization reactor. Otherwise, the unprotected hydroxyl containing moiety would tend to react with the Group VIII metal catalyst, thereby leading to a loss of activity.

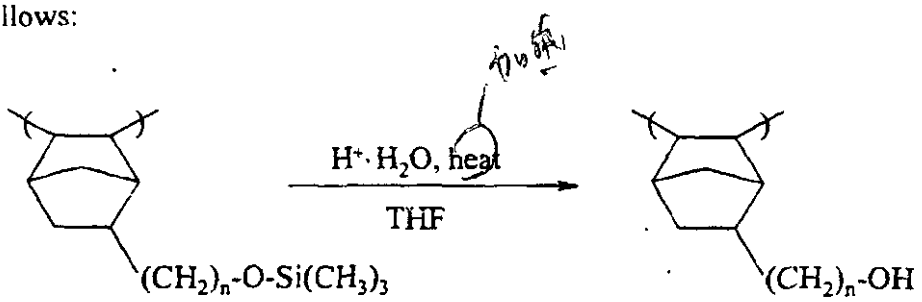
The protecting groups described under G above are introduced into the monomer by techniques well known in the art and are described, for example, in T. W. Green and P. G. M. Wuts, *Protective Groups In Organic Synthesis*, Second Edition, John Wiley & Sons. Inc., New York, 1991. Other protecting groups can be employed so long as they are easily introduced into the monomer, do not interact with the catalyst system so as to inhibit the polymerization reaction, are easily removed from the protected moiety, and do not attack the deprotected moiety. The protecting group should also be able to be selectively removed by deprotection reagents that do not attack the acid labile groups in the base polymer. In other words the protecting group should have a lower activation energy than the acid labile group.

Preferably the protecting group should also have a lower activation energy than the acid labile moiety to ensure that the protecting group is clipped while the acid labile group remains intact.

Following the synthesis of the base polymer containing the desired pendant protected hydroxyl containing moiety, the protected hydroxyl containing moiety is deprotected to yield the alcohol, carboxylic acid or phenol containing functionality. Removal of the protecting groups are well described in the art, for example, see *Protective Groups In Organic Synthesis*, supra. Representative deprotection reactions are set forth below:

Alcohols:

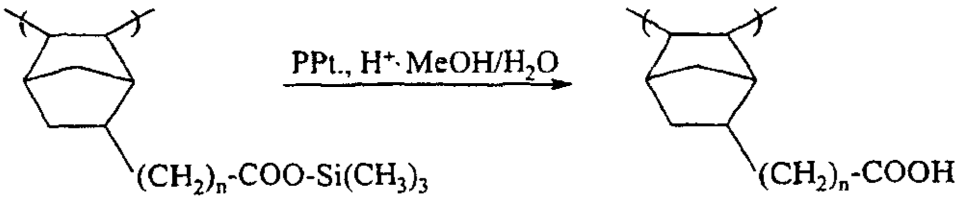
Repeating units containing pendant protected alcohol substituents (silyl ethers) can be deprotected via acid hydrolysis in the presence of tetrahydrofuran solvent as follows:



wherein n is an integer from 0 to 10.

Carboxylic Acids:

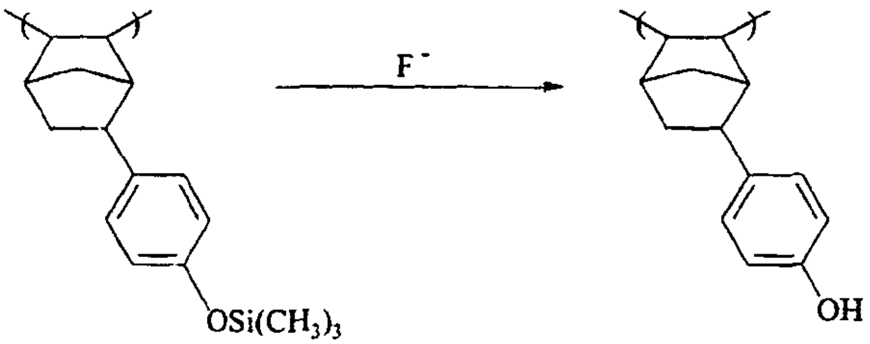
Repeating units containing pendant protected carboxylic acid (silyl esters) substituents can be deprotected via acid hydrolysis as described above or the base polymer containing the repeating unit can be precipitated in an aqueous methanol solution to undergo hydrolysis to the carboxylic acid functionality. A representative deprotection reaction is as follows:



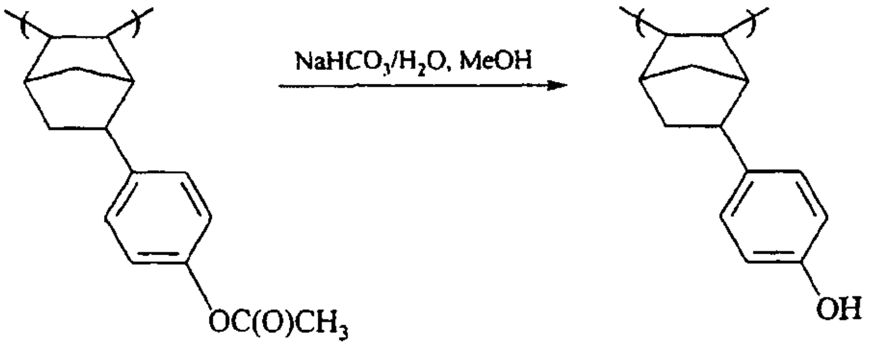
wherein n is an integer from 0 to 10. The acid containing base polymers so produced can be utilized for photoresist applications at this point or can be post-functionalized with a coreactive group as will be described below.

Phenols:

Repeating units containing pendant protected phenol groups (silyl ethers) can be deprotected by refluxing the base polymer containing same in an acidic methanol solution. Trimethylsilyl groups in silyl ether protected groups can be cleaved by mild acids and bases or in the presence of fluoride ion (tetraalkylammonium fluoride). The reaction scheme can be represented as follows:



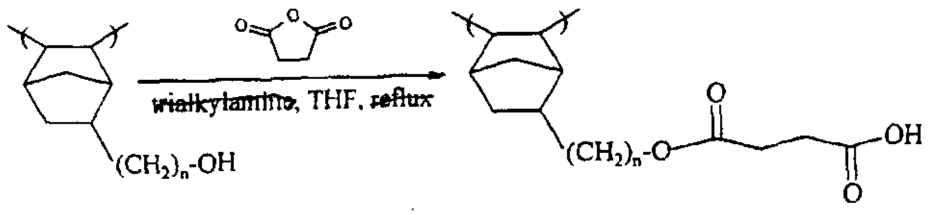
The phenol can also be protected as an phenyl acetate moiety and cleaved to yield the phenol in the presence of aqueous sodium bicarbonate/methanol solution as show below:



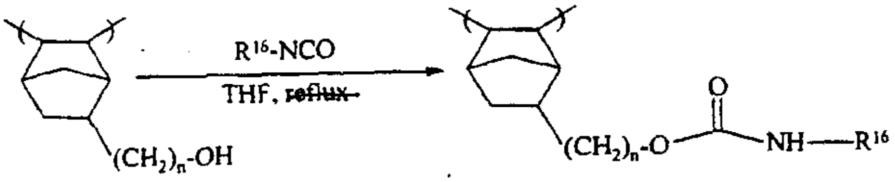
The base polymers of the present invention are post-functionalized through the deprotected alcohol and carboxylic acid groups that are pendant from the polycyclic repeating units in the base polymer. The deprotected base polymers of the invention can be post-functionalized with any coreactive moiety that enhances the properties of the photoresist polymer.

Base polymers containing pendant alcohol groups can be post-functionalized with succinic anhydride, isocyanates of the formula R^{16}-NCO, sulfonate esters of the formula: R^{16}-SO_2-O-SO_2-R^{16} and coreactive moieties of the formula R^{16}-C(O)O(O)C-R^{16} wherein in the above formulae R^{16} is a linear or branched (C_1 to C_{10}) alkyl group, (C_6 to C_{20}) aryl, (C_7 to C_{24}) aralkyl, or a silyl group represented by the formula $-(CH_2)_n-Si(R^{19})_3$, wherein R^{19} is a linear or branched (C_1 to C_{10}) alkyl group, (C_6 to C_{20}) aryl, (C_7 to C_{24}) aralkyl, and n is an integer from 0 to 10. As used here and throughout the specification by aralkyl is meant an aryl group with a linear or branched (C_1 to C_{10}) alkyl substituent(s). Representative aryl and aralkyl groups are phenyl, tolyl, xylyl, and the like. Representative reactions are set forth below:

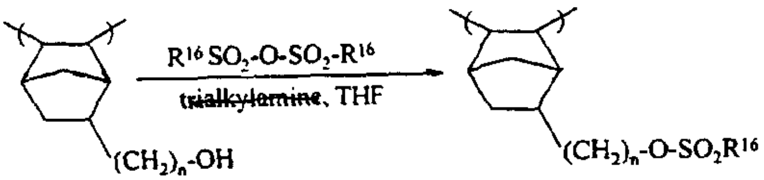
1.


~~trialkylamine~~, THF, ~~reflux~~
(CH2)n-OH
(CH2)n-O
OH
O
O

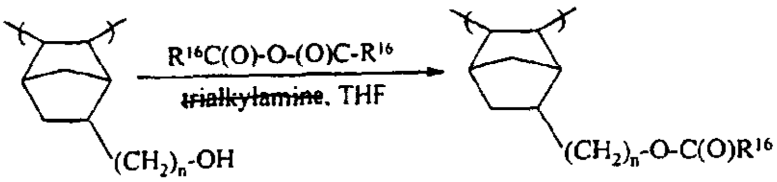
2.


R16-NCO
THF, ~~reflux~~
(CH2)n-OH
(CH2)n-O
O
NH—R16

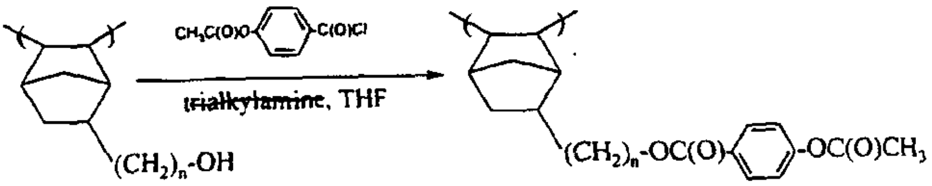
3.


R16 SO2-O-SO2-R16
~~trialkylamine~~, THF
(CH2)n-OH
(CH2)n-O-SO2R16

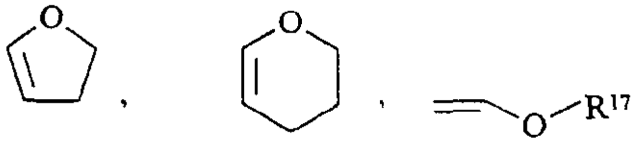
4.


R16C(O)-O-(O)C-R16
~~trialkylamine~~, THF
(CH2)n-OH
(CH2)n-O-C(O)R16

5.

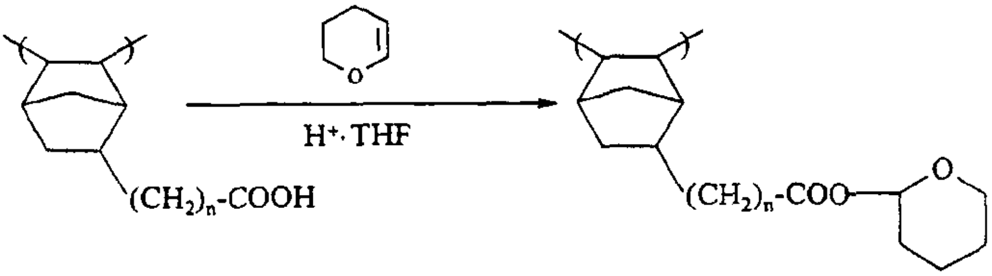

CH3C(O)O- -C(O)Cl
~~trialkylamine~~, THF
(CH2)n-OH
(CH2)n-OC(O)- -OC(O)CH3

Base polymers containing pendant carboxylic acid groups can be post-functionalized with linear and branched acetals, cyclic acetals, orthocarbonates, and vinyl ethers that are coreactive with the carboxylic group. Suitable linear and branched acetal substituents include methoxymethyloxy, ethoxymethyloxy, n-propoxymethyloxy, n-butoxymethyloxy, phenoxymethyloxy, isopropoxymethyloxy, t-butoxymethyloxy, and trichloroethoxymethyloxy groups. Suitable cyclic acetal substituents include tetrahydrofuranyloxy and tetrahydropyranyloxy groups. Suitable orthocarbonate substituents include trimethoxymethyloxy, triethoxymethyloxy tri-n-propoxymethyloxy, and diethoxymethyloxy groups. Enolethers include vinyl ether, 1-propenyl ether, 1-butenyl ether, 1.3-butadienyl ether, and phenylvinyl ether. Representative coreactive moieties are set forth below:

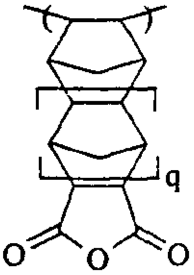


wherein R^{17} represents linear or branched (C_1 to C_{10}) alkyl, (C_2 to C_{10}) alkenyl, or aryl.

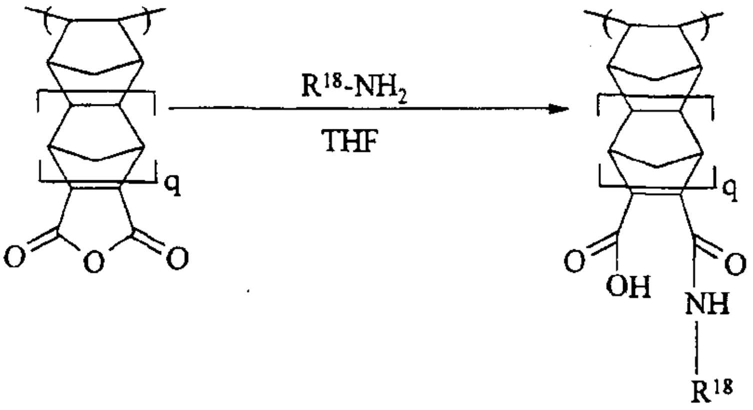
The foregoing moieties are reacted with the desired base polymer comprising repeating units having the pendant carboxylic acid groups. The reaction is conducted in appropriate solvent and at a temperature conducive to effecting the reaction. A typical post-functionalization reaction scheme for the carboxylic acid moiety can be represented as follows:



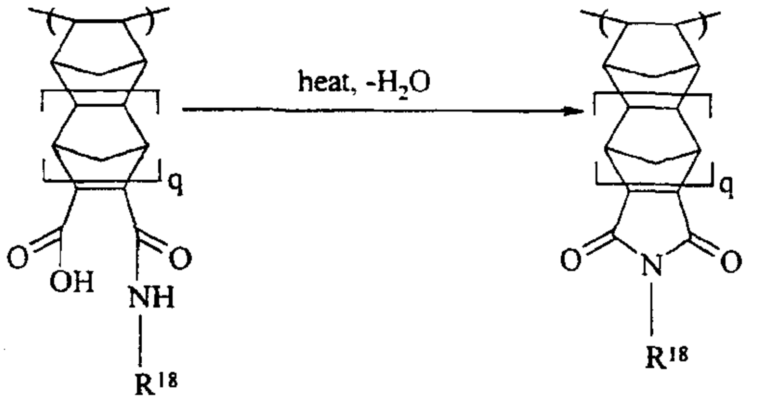
Base polymers comprising repeating units of Formula **I** and Formula **III** can be post-functionalized so long as the substituents on the polycyclic repeat unit of Formula **III** are suitable for post reaction and the post reaction conditions do not deleteriously affect the acid labile group on the Formula **I** corepeat unit. The following Formula **III** functional group wherein R^9 and R^{12} taken with the carbon atoms to which they are attached form a cyclic anhydride has been found to be an excellent platform for post-functionalization reactions.



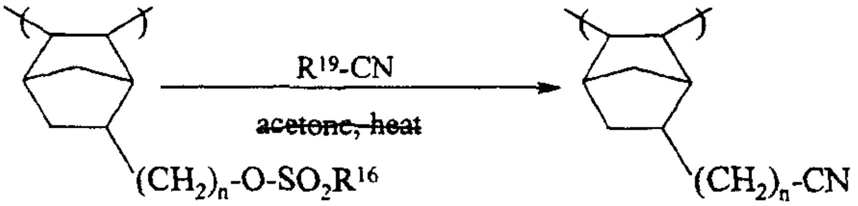
The cyclic anhydride functionality can be reacted with an amine, R^{18}-NH_2, or and alcohol to yield a difunctional acid/amide or difunctional acid/ester. Conversion of the anhydride functionality to the difunctional acid/amide is shown below:



wherein R^{18} is linear or branched (C_1 to C_{10}) alkyl, (C_6 to C_{20}) aryl or aralkyl. The difunctional repeating unit so obtained can be cyclized via a condensation reaction in an appropriate solvent to yield an imide functionality as shown below:

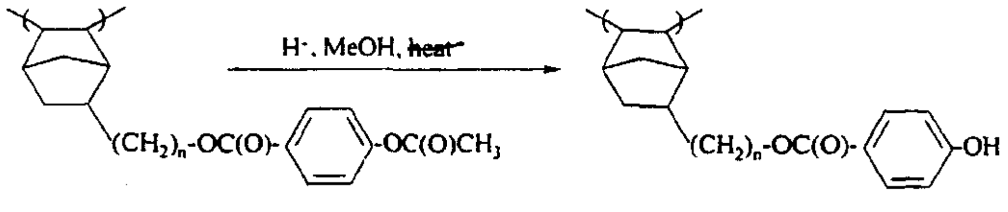


In addition to post-functionalizing desired alcohol and carboxylic acid containing base polymer compositions, it will be recognized that the post-functionalized polymer compositions of this invention can be further functionalized to introduce pendant substituents into the polymer backbone. For example, nitrile groups can be introduced into the polymer by reacting sulfonyl ester substituted polymers with a cyanide salt, e.g., sodium cyanide, or an organonitrile such as trimethylsilylnitrile in the presence of a halide salt to yield a polymer having nitrile substituted repeating units. The reaction can be written as follows:



wherein R^{19} is an organo group capable of being clipped by an halide salt such as sodium chloride, sodium fluoride and the like.

In another reaction the post-functionalized product of equation 5 above can be further reacted to clip the acetate substituent from the phenyl ring in the presence of an acidic methanol solution to obtain the corresponding phenol. The reaction is represented as follows:



The foregoing post-functionalization reactions can be carried out by reacting the base polymer comprising repeating units having the pendant reactive moiety with the desired coreactive moiety in an appropriate solvent and at a temperature that induces the reaction but that does not unduly affect the reactants or desired product. Suitable solvents include aromatic hydrocarbon solvents such as benzene, chlorobenzene, xylene, and toluene; halohydrocarbon solvents such as dichloroethane, methylene chloride, and carbon tetrachloride; acid ethers such as ethyl acetate and butyl acetate; and ethers such as tetrahydrofuran (THF). The choice of solvent will depend on the reactants, and desired reaction conditions. Preferred solvents are ethers such as dioxane and THF. The base polymer or functionalized polymer to be reacted is dissolved in the desired solvent along with the appropriate coreactants. The reactants are then reacted with stirring in an appropriate temperature range to effect an efficient functionalization reaction. Reaction temperatures can range from about -100° C to reflux temperatures depending on the nature of the reaction and solvent. Upon completion of the functionalization, the polymer is separated from the reaction medium and purified in accordance with conventional techniques. The degree of post-functionalization of the hydroxy containing moieties of the invention generally ranges from 10 to 100 mole percent, preferably 20 to 80 mole precent, and more preferably 30 to 70 mole percent.

The photoresist compositions of the present invention comprise the disclosed polycyclic compositions, a solvent, and an photosensitive acid generator (photoinitiator). Optionally, a dissolution inhibitor can be added in an amount of up to about 20 weight % of the composition. A suitable dissolution inhibitor is t-butyl chelate (JV Crivello et al., Chemically Amplified Electron-Beam Photoresists. *Chem. Mater.*, 1996, 8, 376-381).

Upon exposure to radiation, the radiation sensitive acid generator generates a strong acid. Suitable photoacid generators include triflates (e.g., triphenylsulfonium triflate), pyrogallol (e.g., trimesylate of pyrogallol); onium salts such as triarylsulfonium and diaryliodium hexafluoroantimonates, hexafluoroarsenates, trifluoromethanesulfonates; esters of hydroxyimides, α,α'-bis-sulfonyl-diazomethanes, sulfonate esters of nitro-substituted benzyl alcohols and napthoquinone-4-diazides. Other suitable photoacid generators are disclosed in Reichmanis et al., *Chem. Mater.* 3, 395, (1991). Compositions containing triarylsulfonium or diaryliodonium salts are preferred because of their sensitivity to deep UV light (193 to 300 nm) and they give very high resolution images. Most preferred are the unsubstituted and symmetrically or unsymmetrically substituted diaryliodium or triarylsulfonium salts. The photoacid initiator component comprises about 1 to 100 w/w % to polymer. The preferred concentration range is 5 to 50 w/w %.

The photoresist compositions of the present invention optionally contain a sensitizer capable of sensitizing the photoacid initiator to longer wave lengths ranging from mid UV to visible light. Depending on the intended application, such sensitizers include polycyclic aromatics such as pyrene and perylene. The sensitization of photoacid initiators is well-known and is described in U.S. Patent Nos. 4,250,053; 4,371,605; and 4,491,628 which are all incorporated herein by reference. The invention is not limited to a specific class of sensitizer or photoacid initiator.

The present invention also relates to a process for generating a positive tone resist image on a substrate comprising the steps of: (a) coating a substrate with a film comprising the positive tone resist composition of the present invention; (b) imagewise exposing the film to radiation; and (c) developing the image.

The first step involves coating the substrate with a film comprising the positive tone resist composition dissolved in a suitable solvent. Suitable substrates are comprised of silicon, ceramics, polymer or the like. Suitable solvents include propylene glycol methyl ether acetate (PGMEA), cyclohexanone, butyrolactate, ethyl lactate, and the like. The film can be coated on the substrate using art known techniques such as spin or spray coating, or doctor blading. Preferably, before the film has been exposed to radiation, the film is heated to an elevated temperature of about 90°C to 150°C for a short period of time of about 1 min. In the second step of the process, the film is imagewise exposed to radiation suitably electron beam or electromagnetic preferably electromagnetic radiation such as ultraviolet or x-ray, preferably ultraviolet radiation suitably at a wave length of about 193 to 514 nm preferably about 193 nm to 248 nm. Suitable radiation sources include mercury,

mercury/xenon, and xenon lamps, argon fluoride and krypton fluoride lasers, x-ray or e-beam. The radiation is absorbed by the radiation-sensitive acid generator to produce free acid in the exposed area. The free acid catalyzes the cleavage of the acid labile pendant group of the copolymer which converts the copolymer from dissolution inhibitor to dissolution enhancer thereby increasing the solubility of the exposed resist composition in an aqueous base. Preferably, after the film has been exposed to radiation, the film is again heated to an elevated temperature of about 90°C to 150°C for a short period of time of about 1 minute.

The third step involves development of the positive tone image with a suitable solvent. Suitable solvents include aqueous base preferably an aqueous base without metal ions such as tetramethyl ammonium hydroxide or choline. The composition of the present invention provides positive images with high contrast and straight walls. Uniquely, the dissolution property of the composition of the present invention can be varied by simply varying the composition of the copolymer.

The present invention also relates to an integrated circuit assembly such as an integrated circuit chip, multichip module, or circuit board made by the process of the present invention. The integrated circuit assembly comprises a circuit formed on a substrate by the steps of: (a) coating a substrate with a film comprising the positive tone resist composition of the present invention; (b) imagewise exposing the film to radiation; (c) developing the image to expose the substrate; and (d) forming the circuit in the developed film on the substrate by art known techniques.

After the substrate has been exposed, circuit patterns can be formed in the exposed areas by coating the substrate with a conductive material such as conductive metals by art known techniques such as evaporation, sputtering, plating, chemical vapor deposition, or laser induced deposition. The surface of the film can be milled to remove any excess conductive material. Dielectric materials may also be deposited by similar means during the process of making circuits. Inorganic ions such as boron, phosphorous, or arsenic can be implanted in the substrate in the process for making p or n doped circuit transistors. Other means for forming circuits are well known to those skilled in the art.

The following examples are detailed descriptions of methods of preparation and use of certain compositions of the present invention. The detailed preparations fall within the scope of, and serve to exemplify, the more generally described methods of preparation set forth above. The examples are presented for illustrative purposes only, and are not intended as a restriction on the scope of the invention.

Example 1

Synthesis of t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol copolymer (50/50 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 17.6 g (0.089 mol) of trimethylsilyl protected norbornyl alcohol, 17.4 g (0.089 mol) of t-butyl ester of norbornene and 80 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution (monomer to catalyst ratio of 200/1). The catalyst solution was prepared inside a dry box by adding 0.43 g (0.895 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 15 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.255 g of 1,2-cyclohexanedione dioxime dissolved in 10 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex and the filtrate was concentrated and poured into acetone to precipitate the polymer. The precipitated polymer was filtered, redissolved in tetrahydrofuran, and treated with Amberlyst® IR-131 (Rohm & Haas) a polystyrene/sulfonic acid based wet ion exchange resin. The resulting polymer solution was concentrated and precipitated into methanol. The polymer was filtered and dried overnight under vacuum. The yield of polymer was 15.3 g (44%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 47,000, with a Mw of 84,000. IR clearly indicated the absence of any hydroxyl group. ^{1}H NMR indicated the polymer composition was very close to the initial monomer feed ratio.

Example 2

Synthesis of t-butylester of norbornene/norbornyl alcohol copolymer from t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol copolymer (50/50 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 17.6 g (0.089 mol) of trimethylsilyl protected norbornyl alcohol, 17.4 g (0.089 mol) of t-butyl ester of norbornene and 80 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.43 g (0.895 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 15 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.255 g of 1,2-cyclohexanedione dioxime dissolved in 10 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with a small amount of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 21.4 g (61%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 36,000, with a Mw of

68,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 3

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (70/20/10 ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 11.5 g (0.061 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 3.38 g (0.017 mol) of t-butyl ester of norbornene, 1.71 g (8.7 mmol) of trimethylsilyl protected norbornyl alcohol and 40 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.211 g (0.435 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.123 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 16.2 g (95%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 45,000, with a Mw of 85,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 4

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (60/30/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 10.25 g (0.052 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 5.07 g (0.026 mol) of t-butyl ester of norbornene, 1.71 g (8.7 mmol) of trimethylsilyl protected norbornyl alcohol and 40 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.211 g (0.435 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.123 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50 °C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 15.3 g (90%). The polymer was

further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 40,600 with a Mw of 83,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 5

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (50/40/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 25.1 g (0.128 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 19.88 g (0.102 mol) of t-butyl ester of norbornene, 5.02 g (0.026 mol) of trimethylsilyl protected norbornyl alcohol and 40 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.620 g (1.28 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.3636 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 35.9 g (72%). The polymer was

further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 34,600 with a Mw of 68,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 6

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (50/35/15 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 12.5 g (0.638 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 8.68 g (0.045 mol) of t-butyl ester of norbornene, 3.76 g (0.019 mol) of trimethylsilyl protected norbornyl alcohol and 40 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.301 g (0.638 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.181 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 20.00 g (80%). The polymer was

further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 34,300 with a Mw of 72,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 7

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (50/30/20 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 6.5 g (0.338 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 3.86 g (0.019 mol) of t-butyl ester of norbornene, 2.6 g (0.013 mol) of trimethylsilyl protected norbornyl alcohol and 40 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.301 g (0.638 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.181 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 21.23 g (85%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 34,300 with a Mw of 72,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 8

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (50/25/25 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 12.5 g (0.638 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 6.21 g (0.032 mol) of t-butyl ester of norbornene, 6.28 g (0.032 mol) of trimethylsilyl protected norbornyl alcohol and 62 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.309 g (0.64 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.182 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 16.6 g (66%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 41,300 with a Mw of 75,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 9

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (50/25/25 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 12.5 g (0.638 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 6.21 g (0.032 mol) of t-butyl ester of norbornene, 6.28 g (0.032 mol) of trimethylsilyl protected norbornyl alcohol and 62 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.309 g (0.64 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5.0 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.182 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 16.6 g (66%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 41,300 with a Mw of 75,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 10

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (30/50/20 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 4.85 g (0.024 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 8.0 g (0.041 mol) of t-butyl ester of norbornene, 3.23 g (0.016 mol) of trimethylsilyl protected norbornyl alcohol and 30 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.199 g (0.412 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 15 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.117 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at

50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 0.72 g (24%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 19,000 with a Mw of 77,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 12

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (70/20/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 16.02 g (0.071 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate, 3.97 g (0.02 mol) of t-butyl ester of norbornene. 2.00 g (0.01 mol) of trimethylsilyl protected norbornyl alcohol and 55 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.247 g (0.51 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.145 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at

50 °C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 9.7 g (60%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 31,300 with a Mw of 65,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 11

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl acetate/t-butylester of norbornene/norbornyl alcohol terpolymer from bicyclo[2.2.1]hept-5-ene-2-methyl acetate/t-butylester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (40/40/20 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 1.10 g (6.65 mmol) of bicyclo[2.2.1]hept-5-ene-2-methyl acetate, 1.30 g (6.7 mmol) of t-butyl ester of norbornene, and 0.60 g (3.08 mmol) of trimethylsilyl protected norbornyl alcohol. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.04 g (0.083 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 7 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.024 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at

50 °C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 20.3 g (92%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 19,000 with a Mw of 77,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 13

Synthesis of ethyl ester of norbornene/norbornyl alcohol copolymer from ethyl ester of norbornene/trimethylsilyl protected norbornyl alcohol terpolymer (70/20/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 16.05 g (0.02 mol) of ethyl ester of norbornene, 18.96 g (0.097 mol) of trimethylsilyl protected norbornyl alcohol and 90 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.47 g (0.97 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.275 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, a portion of the precipitated polymer was redissolved in tetrahydrofuran with 5 ml of deionized water and treated with Amberlyst® IR-15 dry ion exchange resin at 50 °C for 5 hours. The resulting polymer solution was concentrated and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 28.5 g (81%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 49,000 with a Mw of 80,000. IR clearly indicated the presence of hydroxyl groups. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 14

Conversion of t-butyl ester of norbornene/norbornyl alcohol copolymer to t-butyl ester of norbornene/succinic acid mono (norbornyl methyl)ester copolymer using succinic anhydride (50/50 mole ratio).

To a dry 3-neck 50 ml round bottom flask equipped with a reflux condenser and a thermometer was placed 0.5 g of the t-butyl ester of norbornene/norbornyl alcohol copolymer obtained from Example 2, followed by 0.014 g (0.14 mmol) of succinic anhydride, 10 ml of tetrahydrofuran and 4.2 μl (0.028 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene. The mixture was refluxed for 3 hours and then was diluted with dimethylformamide (DMF) and precipitated into a dilute acetic acid solution. The precipitated polymer was washed with methanol, to remove any unreacted succinic anhydride, filtered and dried overnight under vacuum. The polymer was characterized using IR and NMR. The mol. wt. of the polymer was observed to be Mn = 49,000 with a Mw of 80,000. Both IR and ^{1}H clearly indicated the presence of acid functionality group.

Example 15

Conversion of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer to bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/succinic acid mono (norbornyl methyl)ester copolymer using succinic anhydride (50/30/20 mole ratio).

To a dry 3-neck 50 ml round bottom flask equipped with a reflux condenser and a thermometer was placed 0.5 g of the bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer obtained from Example 7, followed by 0.042 g (0.14 mmol) of succinic anhydride, 10 ml of tetrahydrofuran and 57 1 (0.379 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene. The mixture was refluxed for 3 hours and then cooled. The polymer was precipitated into a dilute acetic acid solution. The precipitated polymer was washed with methanol to remove any unreacted succinic anhydride, filtered and dried overnight under vacuum. The polymer was further characterized using IR and NMR. IR clearly indicated the conversion of hydroxyl functionality to acid functionality.

Example 16

Conversion of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer to bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/succinic acid mono (norbornyl methyl)ester copolymer using succinic anhydride (50/40/10 mole ratio).

To a dry 3-neck 50 ml round bottom flask equipped with a reflux condenser and a thermometer was placed 0.5 g of the bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer obtained from Example 5, followed by 0.73 g (7.3 mmol) of succinic anhydride, 35 ml of tetrahydrofuran and 325 1 (2.18 mmol) of 1,8-diazabicyclo[5.4.0]undec-

7-ene. The mixture was refluxed for 3 hours after which the solution was cooled, diluted with tetrahydrofuran, and the polymer was precipitated into a dilute acetic acid solution. The precipitated polymer was washed with methanol to remove any unreacted succinic anhydride, filtered and dried overnight under vacuum. The polymer was further characterized using IR and NMR. IR clearly indicated the conversion of hydroxyl functionality to acid functionality.

Example 17

Conversion of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer to bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/succinic acid mono (norbornyl methyl)ester copolymer using succinic anhydride (50/35/15 mole ratio).

To a dry 3-neck 250 ml round bottom flask equipped with a reflux condenser and a thermometer was placed 16.6 g of the bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer obtained from Example 6, followed by 1.58 g (0.016 mol) of succinic anhydride, 100 ml of tetrahydrofuran and 710 l (4.75 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene. The mixture was refluxed for 3 hours after which the solution was cooled, diluted with tetrahydrofuran and the polymer was precipitated into a dilute acetic acid solution. The precipitated polymer was washed with methanol to remove any unreacted succinic anhydride, filtered and dried overnight under vacuum. The dried polymer was dissolved in tetrahydrofuran, and treated with Amberlyst® IR-15 dry ion exchange resin, filtered, concentrated and precipitated into methanol. The polymer was characterized using IR and NMR and GPC. IR clearly indicated the conversion of hydroxyl functionality to acid functionality. The mol. wt. of the polymer was measured to be Mn = 32,000 and Mw = 84,000.

Example 18

Conversion of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer to bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/succinic acid mono (norbornyl methyl)ester copolymer using succinic anhydride (50/25/25 mole ratio).

To a dry 3-neck 250 ml round bottom flask equipped with a reflux condenser and a thermometer was placed 14.5 g of the bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butyl ester of norbornene/norbornyl alcohol terpolymer obtained from Example 8, followed by 0.83 g (8.27 mmol) of succinic anhydride, 100 ml of tetrahydrofuran and 370 l (2.48 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene. The mixture was refluxed for 3 hours after which the solution was cooled, diluted with dimethylformamide, and the polymer was precipitated into a dilute acetic acid solution. The precipitated polymer was washed with methanol to remove any unreacted succinic anhydride and dried overnight under vacuum. The dried polymer was dissolved in tetrahydrofuran, and treated with Amberlyst® IR-15 dry ion exchange resin, filtered, concentrated, and precipitated into methanol. The polymer was further characterized using IR and NMR and GPC. IR clearly indicated the conversion of hydroxyl functionality to acid functionality. The mol. wt. of the polymer was measure to be Mn = 43,000 and Mw = 86,000.

Example 19

Conversion of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/t-butyl ester of norbornene/norbornyl alcohol terpolymer to bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/t-butyl ester of norbornene/succinic acid mono (norbornyl methyl)ester copolymer using succinic anhydride (50/25/25 mole ratio).

To a dry 3-neck 250 ml round bottom flask equipped with a reflux condenser and a thermometer was placed 16.0 g of the bicyclo[2.2.1]hept-5-ene-

2-methyl ethyl oxalate/t-butyl ester of norbornene/norbornyl alcohol terpolymer obtained from Example 12, followed by 2.0 g (0.02 mol) of succinic anhydride, 100 ml of tetrahydrofuran and 897 1 (6.0 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene. The mixture was refluxed for 3 hours after which the solution was cooled, and the polymer was precipitated into a dilute acetic acid solution. The precipitated polymer was washed with methanol, to remove any unreacted succinic anhydride, filtered, and dried overnight under vacuum. The dried polymer was dissolved in tetrahydrofuran, and treated with Amberlyst® IR-15 dry ion exchange resin, filtered, concentrated, and precipitated into methanol. The polymer was characterized using IR and NMR and GPC. IR clearly indicated the conversion of hydroxyl functionality to acid functionality. The mol. wt. of the polymer was measure to be Mn = 68,000 and Mw = 149,000.

Example 20

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/t-butylester of norbornene/norbornyl carboxylic acid terpolymer from terpolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/t-butylester of norbornene/trimethylsilyl ester of norbornene (50/40/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 14.00 g (0.063 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate, 9.70 g (0.05 mol) of t-butyl ester of norbornene, 2.63 g (0.013 mol) of trimethylsilyl ester of norbornene and 65 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.303 g (0.62 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.178 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, the precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into methanol. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 13.4 g (51%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 33,000 with a Mw of 85,000. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 21

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/norbornyl carboxylic acid copolymer from copolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate/trimethylsilyl ester of norbornene (50/50 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 1.03 g (4.6 mmol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl oxalate, 0.962 g (4.57 mmol) of trimethylsilyl ester of norbornene, followed by 5 ml of cyclohexane and 1 ml of ethyl acetate. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.022 g (0.046 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5 ml of toluene. The polymerization was allowed to stir for 5 hours and the solution was poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, the precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The overall yield of polymer was 0.64 g (32%). The polymer was characterized using GPC, IR and NMR. The mol. wt of the polymer was observed to be Mn = 49,000 with a Mw of 142,000. IR clearly indicated the presence of acid functionality and the polymer composition was very close to the initial monomer feed ratio via ^{1}H NMR.

Example 22

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid terpolymer from terpolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene (50/40/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 21.00 g (0.11 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 16.6 g (0.085 mol) of t-butyl ester of norbornene, 4.5 g (0.021 mol) of trimethylsilyl ester of norbornene and 430 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.038 g (2.14 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.61 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, the precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was concentrated and precipitated into a 1N acetic acid/methanol solution. The resulting polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 31 g (75%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 18,000 with a Mw of 36,000. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 23

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid terpolymer from terpolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene (40/40/20 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 17.94 g (0.191 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 17.76 g (0.091 mol) of t-butyl ester of norbornene, 9.6 g (0.046 mol) of trimethylsilyl ester of norbornene and 288 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.108 g (2.28 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.65 g of 1,2-cyclohexanedione dioxime dissolved in 5 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, the precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 29 g (64%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 17,000 with a Mw of 33,700. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 24

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid terpolymer from terpolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene (50/25/25 mole ratio.

To a glass vial containing a stir bar was added under nitrogen atmosphere 19.74 g (0.1 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 9.75 g (0.501 mol) of t-butyl ester of norbornene, 10.56 g (0.050 mol) of trimethylsilyl ester of norbornene and 253 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 0.973 g (2.01 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which the polymer solution was treated with Amberlite® IRC-718 (Rohm & Haas) imidoacetic acid based chelating resin, followed by Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 27.6 g (68%). The polymer was characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 19,000 with a Mw of 41,700. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 25

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid terpolymer from terpolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene (50/35/15 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 21.34 g (0.11 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 14.8 g (0.076 mol) of t-butyl ester of norbornene, 6.86 g (0.033 mol) of trimethylsilyl ester of norbornene and 273 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.055 (2.17 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which the polymer solution was treated with Amberlite® IRC-718 chelating resin, followed by Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 31.6 g (74%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 19,000 with a Mw of 40,000. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 26

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid/ethyl ester of tetracyclododecene tetrapolymer from tetrapolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene/ethyl ester of tetracyclododecene (25/35/15/25 mole ratio.

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To a glass vial containing a stir bar was added under nitrogen atmosphere 10.68 g (0.052 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 12.64 g (0.054 mol) ethyl ester of tetracyclododecene, 14.08 g (0.076 mol) of t-butyl ester of norbornene, 6.86 g (0.033 mol) of trimethylsilyl ester of norbornene and 110 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.055 g (2.17 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which the polymer solution was treated with Amberlite® IRC-718 chelating resin, followed by Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 27.9 g (62%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 12,000 with a Mw of 26,000. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 27

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid/ethyl ester of tetracyclododecene tetrapolymer from tetrapolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene/ethyl ester of tetracyclododecene (25/25/25/25 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 11.78 g (0.06 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 13.94 g (0.06 mol) ethyl ester of tetracyclododecene, 11.66 g (0.06 mol) of t-butyl ester of norbornene, 12.6 g (0.06 mol) of trimethylsilyl ester of norbornene and 110 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.16 g (2.17 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which the polymer solution was treated with Amberlite® IRC-718 chelating resin, followed by Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 26.1 g (52%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 12,000 with a Mw of 26,000. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 28

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid/bicyclo[2.2.1]hept-5-ene-methyl ethyl oxalate tetrapolymer from tetrapolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene/bicyclo[2.2.1]hept-5-ene-methyl ethyl oxalate (30/30/30/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 10.31 g (0.053 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 11.78 g (0.052 mol) bicyclo[2.2.1]hept-5-ene-methyl ethyl oxalate, 10.21 g (0.052 mol) of t-butyl ester of norbornene, 3.68 g (0.017 mol) of trimethylsilyl ester of norbornene and 110 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 0.849 g (1.75 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which the polymer solution was treated with Amberlite® IRC-718 chelating resin, followed by Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 29.1 g (81%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 25,000 with a Mw of 68,000. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was very close to the initial monomer feed ratio.

Example 29

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid/bicyclo[2.2.1]hept-5-ene-2-methyl methylether tetrapolymer from tetrapolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene/bicyclo[2.2.1]hept-5-ene-methyl methylether (30/30/30/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 13.11 g (0.067 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 9.23 g (0.067 mol) bicyclo[2.2.1]hept-5-ene-2-methyl methylether, 12.98 g (0.067 mol) of t-butyl ester of norbornene, 4.68 g (0.022 mol) of trimethylsilyl ester of norbornene and 110 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.08 g (2.23 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.63 g of 1,2-cyclohexanedione dioxime dissolved in 10 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, the precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 31.7 g (79%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 18,000 with a Mw of 35,700. IR clearly indicated the presence of acid functionality. ^{1}H NMR indicated the absence of trimethylsilyl groups and the polymer composition was found to be very close to the initial monomer feed ratio.

Example 30

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid/bicyclo[2.2.1]hept-5-ene tetrapolymer from tetrapolymer of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/trimethylsilyl ester of norbornene/bicyclo[2.2.1]hept-5-ene (50/30/10/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 20.99 g (0.107 mol) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 2.01 g (0.021 mol) bicyclo[2.2.1]hept-5-ene, 12.47 g (0.064 mol) of t-butyl ester of norbornene, 4.5 g (0.021 mol) of trimethylsilyl ester of norbornene and 110 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 100/1. The catalyst solution was prepared inside a dry box by adding 1.03 g (2.14 mmol) of

$(CH_3C_6H_5)Ni(C_6F_5)_2$ in 10 ml of toluene. The polymerization was allowed to stir for 5 hours after which a solution of 0.61 g of 1,2-cyclohexanedione dioxime dissolved in 10 ml of acetone was added to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. In order to remove the trimethylsilyl protecting group, the precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 34.5 g (86%). The polymer was further characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 20,000 with a Mw of 46,700. IR clearly indicated the presence of acid functionality. ^1H NMR indicated the absence of trimethylsilyl groups and the polymer composition was found to be very close to the initial monomer feed ratio.

Example 31

Introduction of tetrahydropyranyl protecting group from bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate/t-butylester of norbornene/norbornyl carboxylic acid terpolymer (50/25/25 mole ratio).

Into a 50 ml flask containing a stir bar is added under nitrogen atmosphere 5 g of carboxylic acid terpolymer obtained from Example 24, 3 gms of Amberlyst® IR-15 dry ion exchange resin and 15 ml of tetrahydrofuran. To the reaction solution at room temperature is added via syringe 8 ml of dihydropyran. The solution is slowly heated to reflux for 5 hours. The resulting polymer solution is cooled, filtered, concentrated, and precipitated into hexane. The precipitated polymer is filtered and dried overnight under vacuum. The resin obtained is analyzed via IR. The acid functionality in the polymer is expected to undergo an esterification reaction to yield a tetrahydropyranyloxycarbonyl group.

Example 32

Synthesis of bicyclo[2.2.1]hept-5-ene-2-methyl carbonate/t-butylester of norbornene/endonadic anhydride terpolymer and post modification of anhydride functionality to aliphatic imide functionality (50/40/10 mole ratio).

To a glass vial containing a stir bar was added under nitrogen atmosphere 1.56 g (7.95 mmol.) of bicyclo[2.2.1]hept-5-ene-2-methyl ethyl carbonate, 12.64 g (0.054 mmol) ethyl ester of tetracyclododecene, 1.23 g (6.36 mmol) of t-butyl ester of norbornene, 0.26 g (1.59 mmol) of freshly dried endonadic anhydride in 5 ml of toluene. To the reaction solution at room temperature was added via syringe a nickel catalyst solution in a monomer to catalyst ratio of 200/1. The catalyst solution was prepared inside a dry box by adding 0.0383 g (0.08 mmol) of $(CH_3C_6H_5)Ni(C_6F_5)_2$ in 5 ml of toluene. The polymerization was allowed to stir for 5 hours after which the polymer solution was treated with 0.023 g of 1,2-cyclohexanedione dioxime dissolved in 10 ml of acetone, to chelate the Ni catalyst. The chelated Ni complex was observed to precipitate immediately. The solution was stirred overnight, filtered to remove the chelated complex, and the filtrate was concentrated and finally poured into methanol to precipitate the polymer. The precipitated polymer was redissolved in tetrahydrofuran and treated with Amberlyst® IR-15 dry ion exchange resin at 50°C for 5 hours. The resulting polymer solution was filtered, concentrated, and precipitated into hexane. The precipitated polymer was filtered and dried overnight under vacuum. The overall yield of polymer was 1.1 g (36%). The polymer was characterized using GPC, IR and NMR. The mol. wt. of the polymer was observed to be Mn = 23,000 with a Mw of 49,000. IR clearly indicated the presence of anhydride functionality. ^1H NMR indicated the polymer composition was very close to the initial monomer feed ratio.

Example 33

The polymer obtained in Example 32 is further post functionalized to amic acid by reacting with aliphatic amines such as cyclohexyl amine. Into a 50 ml flask containing a stir bar is added under nitrogen atmosphere 1 g of anhydride containing terpolymer and 15 ml of tetrahydrofuran. To the reaction solution at room temperature is added via syringe 5 ml of cyclohexyl amine. The solution is stirred at room temperature for 5 hours. The resulting polymer solution is cooled, and chemically imidized using acetic anhydride, pyridine mixture at 60°C, and is precipitated into methanol. The precipitated polymer is filtered and dried overnight under vacuum.

Example 34

Reaction of 4-hydroxybenzyl alcohol with poly(norbornene methanol-co-t-butyl ester of norbornene) (50/50 mole ratio).

To a 100 ml round-bottom flask containing a stir bar was added 1.35 g of copolymer and 20 ml of THF. Once the polymer was dissolved, 4-hydroxybenzyl alcohol (0.67 g, 5 mmol) was added. The reactants were stirred at room temperature for 10 minutes to ensure complete dissolution. The HCL (4 drops) was added to the solution. The reaction was allowed to stir for 20 hours at room temperature. The polymer was isolated by precipitating into water, filtering, and drying in a vacuum oven set at 80°C for 24 hours. The yield of the resulting polymer was quantitative. NMR and IR confirmed the attachment of the benzyl group to the polymer.

Example 35

Reaction of 1-adamantane isocyanate with poly(norbornene methanol-co-t-butyl ester of norbornene) (50/50 mole ratio).

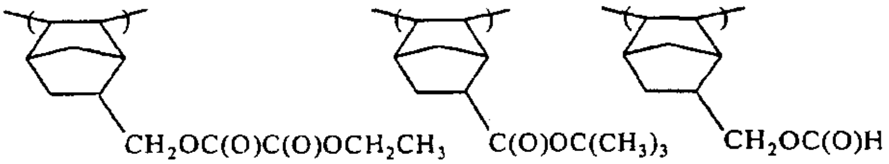
Poly(norbornene methanol-co-t-butyl ester of norbornene) (2 g) and 1-adamantane isocyanate (1.4 g) were added to a 100 ml round-bottom flask. The solids were dissolved in THF (30 ml) and the flask fitted with a reflux condenser, stir bar, and positive nitrogen inlet. The resulting clear colorless solution was refluxed for 5 hours. Then the flask was allowed to cool to room temperature, the contents precipitated into water (200 ml), filtered, and dried in vacuum for 24 hours. Yield = 2.66 g.

The following examples demonstrate that a number of imaging factors can be improved with the post-functionalization addition of pendant carboxylic acid groups to the polycyclic backbone. Resist formulations were prepared as follows: The exemplified polymers and a photoacid generator were dissolved in the casting solvent propylene glycol methyl ether acetate (PGMEA). The resist formulations were spin coated onto silicon wafers and baked a 130°C for 1 minute. The coated wafers were then exposed through a binary mask at 193 nm in the ISI ArF Microstep 0.6 NA. After exposure the wafers were baked a second time at 150°C for 1 minute and developed for 20 seconds with a 0.21N tetramethylammoniumhydroxide (TMAH) solution.

Example 36

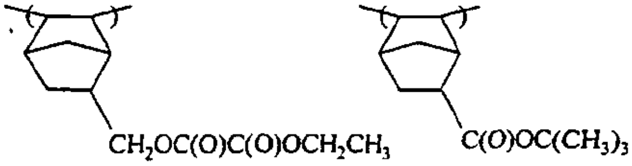
Resist compositions and coated wafers were prepared as described above except that the temperature of the first bake for the copolymer devoid of carboxylic acid moieties was 150°C. An SEM micrograph of an imaged and developed photoresist polymer containing a carboxylic acid moiety introduced by post-functionalization was compared to an SEM micrograph of a photoresist polymer devoid of a carboxylic acid containing moieties. The carboxylic acid containing polymer was the terpolymer obtained in Example 20 containing repeating units having pendant oxalate/t-butyl ester/acid groups in a mole percent ratio of 50/40/10. The terpolymer is represented as follows:

oxalate/t-butyl ester/carboxylic acid containing terpolymer 50/40/10



The polymer devoid of carboxylic functionality was a copolymer containing repeating units having pendant oxalate/t-butyl ester groups in a mole percent ratio of 50/50. The copolymer is represented below:

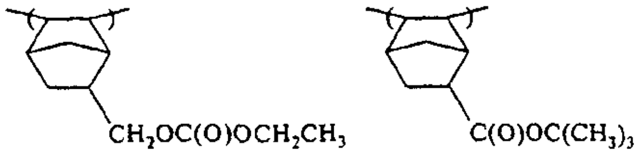
oxalate/t-butyl ester copolymer 50/50



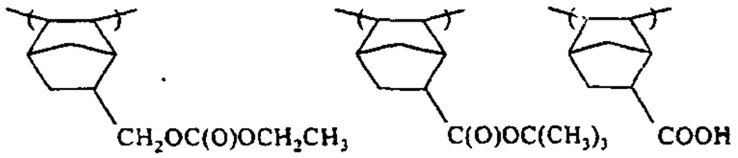
As shown in Fig. 1, the imaged 50/40/10 resist terpolymer at 0.15 micron feature size exhibits clean development and sharp resolution . In sharp contrast, as shown ~~in Fig. 2, the~~ 50/50 copolymer at a relatively higher 0.3 micron feature size, exhibits very rough development with scum visible in the large pads of exposed areas.

Example 37

In this example a copolymer devoid of carboxylic acid functionality containing repeating units having pendant carbonate groups and pendant t-butyl ester groups (50/50 mole percent) was compared to terpolymers containing repeating units having pendant carbonate/t-butyl ester/carboxylic acid groups of 50/40/20 mole percent and 40/40/20 mole percent. Imaging experiments and contact angle measurements of the polymers were conducted as set forth below. The polymers are represented below:



carbonate/t-butyl ester copolymer 50/50



carbonate/t-butyl ester/carboxylic acid containing terpolymer 50/40/10 and 40/40/20

Through the post-functionalization incorporation of carboxylic acid functionality into the polymer backbone the dissolution properties and hydrophilicity of the polymer can be controlled. The contact angle between the surface of each polymer and a droplet of water was measured and is reported in the table below. Contact angle is a good indicator of the hydrophilicity of the polymer.

Contact angle measurements were determined as follows:

The polymers were dissolved in PGMEA and then filtered through a 0.45 micron Teflon® membrane. The filtered solution was spin-coated onto a clean silicon wafer and baked at 140°C for 2 minutes to dry the film.

The coated wafers were placed on AST Products VCA video contact angle goniomiter which measures the angle of the tangency of the droplet profile to the surface of the polymer film. Pure water (2 µl) was syringed onto the surface of the coated wafer using a high precision syrine pump. The water droplet contact angle was measured within 2 or 3 seconds of placing the droplet on the coated wafer surface. Duplicate tests were run for each sample to ensure accuracy.

Polymer Composition Carbonate/t-butyl ester/Acid	Mole % of Repeating Unit Containing Acid Functionality	Contact Angle	Polymer Example
50/50/0	0	78°	----
50/40/10	10	74°	22
40/40/20	20	69°	23

The contact angle correlated well with observations of greatly enhanced wetting during lithography processing. The lower the contact angle, the better the hydrophilic properties of the polymer.

The polymers were formulated into resist compositions and imaged as set forth above. The results of the imaging experiments demonstrated the enormous impact of the post-functionalization incorporation of carboxylic functionality on lithography performance. The 50/50 copolymer (devoid of carboxylic acid functionality) showed a high level of scum, adhesion loss, and poor imaging. Images below .45 microns were not obtainable (Fig. not included). Upon the addition of a carboxylic acid containing moiety (i.e., the 50/40/10 polymer of Example 22), a significant lowering of feature sizes was possible. Figs. 3 and 4 show SEM micrographs of 1:1 pitched 0.15 micron and 2:1 pitched 0.12 micron images, respectively, of the polymer of Example 22. Pitch is the ratio of the spacing between the feature lines to the width of the feature lines. As is illustrated in these figures, well defined, clean images were printed.

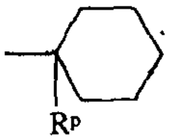
Upon the addition of more carboxylic acid containing moiety (i.e., the 40/40/20 polymer of Example 23), the imaging was improved even further. As shown in Fig. 5 (0.16 micron feature size at 1:1 pitch), the feature profiles became much sharper and the bottoms of the features were much cleaner (less scum). Fig. 6 (0.10 micron feature size at 3:1 pitch) demonstrates that even smaller features are easily printed.

These examples demonstrate that increased hydrophilicity brought about by the post-functionalization incorporation of carboxylic acid containing moieties, leads to vast increases in imaging quality, both in feature sizes and profile aesthetics.

What is claimed is:

1. A polymer containing a cyclic backbone said backbone comprises a pendant acid labile functional group and a protected functional group containing a protected hydroxyl moiety.

2. The polymer of claim 1 wherein said pendant acid labile functional group is terminated with an ester moiety containing an acid labile group selected from Dcpm, Dmcp, -$C(CH_3)_3$, -$CH(R^p)OCH_2CH_3$, -$CH(R^p)OC(CH_3)_3$, and the cyclic group:



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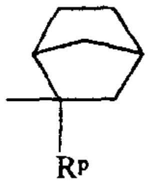

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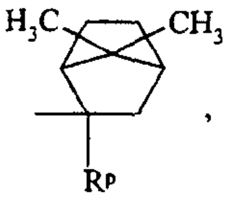

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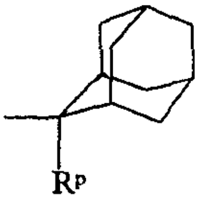

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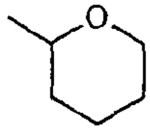

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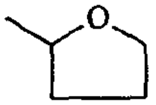

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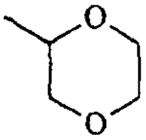
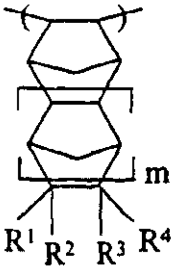


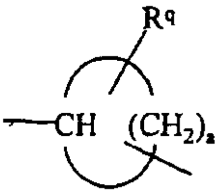
or mixtures thereof, wherein R^p represents hydrogen and a linear or branched (C_1 to C_5) alkyl group; and said protected functional group contains a silyl protected hydroxyl moiety.

3. The polymer of claim 2 wherein said protected functional group is represented by a radical of the formula -$(CH_2)_nOG$, -$(CH_2)_nC(O)OG'$, and -$(CH_2)_n$-(C_6 to C_{14})aryl-OG wherein n is an integer from 0 to 10 and G is a silyl protecting group of the formula -$Si(R^{15})_3$ wherein R^{15} independently represents linear and branched (C_1 to C_{10}) alkyl, (C_6 to C_{14}) aryl, and substituted (C_6 to C_{14}) aryl wherein said substituents are selected form linear and branched (C_1 to C_5) alkyl groups; and G'represents G or -$C(O)CH_3$.

4. A polymer comprising cyclic repeating units wherein a portion of said repeating units contain pendant acid labile groups and another portion of said repeating units contain pendant protected functional groups, said acid labile containing repeating units are represented by the structure:



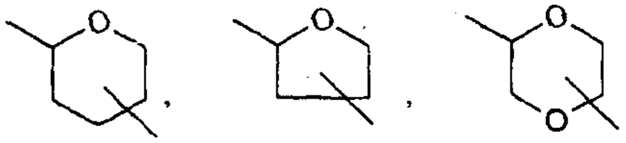
m is an interger from 0 to 10, wherein R^1 to R^4 independently represent a substituent selected from the group $-(A)_nC(O)OR^*$, $-(A)_n-C(O)OR$, $-(A)_n-OR$, $-(A)_n-OC(O)R$, $-(A)_n-C(O)R$, $-(A)_n-OC(O)OR$, $-(A)_n-OCH_2C(O)OR^*$, $-(A)_n-C(O)O-A'-OCH_2C(O)OR^*$, $-(A)_n-OC(O)-A'-C(O)OR^*$, $-(A)_n-C(R)_2CH(R)(C(O)OR^{**})$, and $-(A)_n-C(R)_2CH(C(O)OR^{**})_2$ subject to the proviso that at least one of R^1 to R^4 is selected from an acid labile group containing R^*; A and A′ independently represent a divalent bridging or spacer radical selected from divalent hydrocarbon radicals selected from linear and branched (C_1 to C_{10}) alkylene; divalent cyclic hydrocarbon radicals selected from substituted and unsubstituted (C_3 to C_8) cycloaliphatic moieties of the formula:



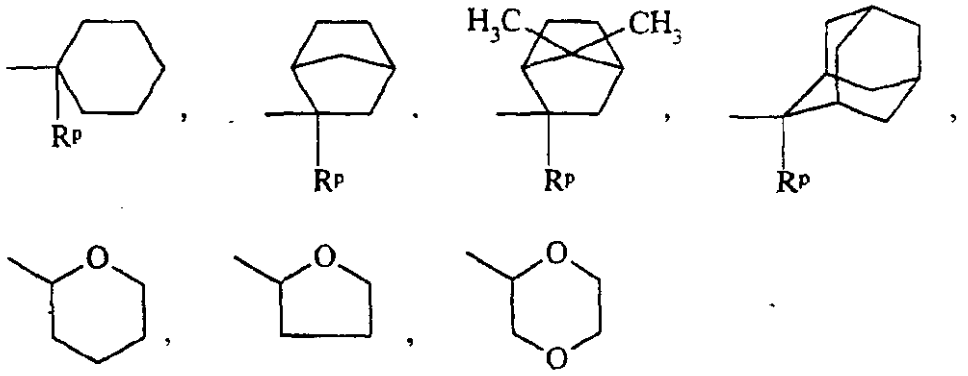
wherein "a" is an integer from 2 to 7 and R^q if present represents linear and branched (C_1 to C_{10}) alkyl groups; divalent oxygen containing radicals selected from (C_2 to C_{10}) alkylene ethers and polyethers of the formula:

$$-\!\!\left(CH_2(CH_2)_xO\right)_{y}\!\!-$$

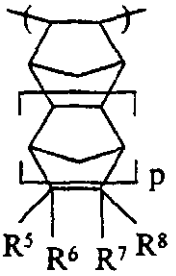
wherein x is an integer from 1 to 5 and y is an integer from 2 to 50, with the proviso that the terminal oxygen atom on the polyether spacer moiety can not be directly linked to a terminal oxygen atom on an adjacent group to form a peroxide linkage; and divalent cyclic ethers and cyclic diethers represented by the structures:



and R^* is acid labile group selected from Dcpm, Dmcp, $-C(CH_3)_3$, $-CH(R^p)OCH_2CH_3$, $-CH(R^p)OC(CH_3)_3$, and the cyclic group:

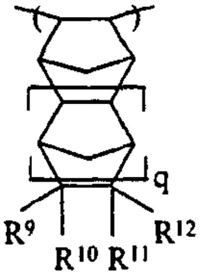


or mixtures thereof, wherein R^p represents hydrogen and a linear or branched (C_1 to C_5) alkyl group; and said protected functional group containing repeating units are represented by the structure:



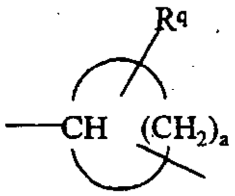
wherein p is an integer from 0 to 5; R^5 to R^8 independently represent hydrogen, linear and branched (C_1 to C_{20}) alkyl, $-(CH_2)_nC(O)OR$, $-(CH_2)_nOR$, $-(CH_2)_nOC(O)R$, $-(CH_2)_nC(O)R$, $-(CH_2)_nOC(O)OR$, wherein R is linear or branched (C_1 to C_{10}) alkyl subject to the proviso that at least one of R^5 to R^8 is selected from a protected functional group represented by $-(CH_2)_nOG$, $-(CH_2)_nC(O)OG$, and $-(CH_2)_n-(C_6$ to $C_{14})$aryl-OG′, wherein n is an integer from 0 to 10, and G is a protecting group selected from the radical $-Si(R^{15})_3$, wherein R^{15} independently represents linear and branched (C_1 to C_{10}) alkyl, (C_6 to C_{14}) aryl, substituted (C_6 to C_{14}) aryl wherein said substituents are selected form linear and branched (C_1 to C_5) alkyl groups, and G′represents G or $-C(O)CH_3$.

5. The polymer of claim 4 further comprising a repeating unit represented by the structure:



wherein q is an integer from 0 to 5; R^9 to R^{12} independently represent hydrogen, linear or branched (C_1 to C_{10}) alkyl, or a substituent selected from the group $-(A)_n-C(O)OR''$, $-(A)_n-OR''$, $-(A)_n-OC(O)R''$, $-(A)_n-OC(O)OR''$, $-(A)_n-C(O)R''$, $-(A)_n-OC(O)C(O)OR''$, $-(A)_n-O-A'-C(O)OR''$,

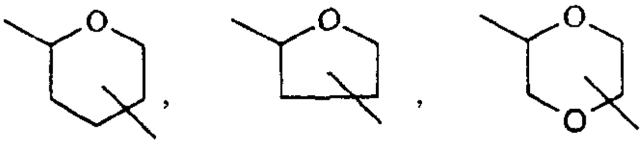
$-(A)_n-OC(O)-A'-C(O)OR''$, $-(A)_n-C(O)O-A'-C(O)OR''$, $-(A)_n-C(O)-A'-OR''$, $-(A)_n-C(O)O-A'-OC(O)OR''$, $-(A)_n-C(O)O-A'-O-A'-C(O)OR''$, $-(A)_n-C(O)O-A'-OC(O)C(O)OR''$, $-(A)_n-C(R'')_2CH(R'')(C(O)OR'')$, and $-(A)_n-C(R'')_2CH(C(O)OR'')_2$, R^9 and R^{12} can be taken together with the ring carbon atoms to which they are attached to represent a cyclic anhydride group; A and A′ independently represent a divalent bridging or spacer radical selected from divalent hydrocarbon radicals selected from linear and branched (C_1 to C_{10}) alkylene; divalent cyclic hydrocarbon radicals selected from substituted and unsubstituted (C_3 to C_8) cycloaliphatic moieties of the formula:



wherein "a" is an integer from 2 to 7 and R^q if present represents linear and branched (C_1 to C_{10}) alkyl groups; divalent oxygen containing radicals selected from (C_2 to C_{10}) alkylene ethers and polyethers of the formula:

$$-\!\left(CH_2(CH_2)_xO\right)_y\!-$$

wherein x is an integer from 1 to 5 and y is an integer from 2 to 50, with the proviso that the terminal oxygen atom on the polyether spacer moiety can not be directly linked to a terminal oxygen atom on an adjacent group to form a peroxide linkage; and divalent cyclic ethers and cyclic diethers represented by the structures:



R″ independently represents, linear and branched (C_1 to C_{10}) alkyl, linear and branched (C_1 to C_{10}) alkoxyalkylene, polyethers, monocyclic and polycyclic (C_4 to C_{20}) cycloaliphatic moieties, cyclic ethers, cyclic ketones, and cyclic esters.

6. A method for post-functionalizing a polymer containing cyclic repeating units comprising the steps of:

a) providing a base polymer comprising cyclic repeating units containing pendant acid labile functional groups and cyclic repeating units containing pendant functional groups containing protected hydroxyl moieties;

b) deprotecting the protected hydroxyl moieties to give functional groups containing a free hydroxyl group;

c) reacting the free hydroxyl group with a coreactive moiety to give a post-functionalized polymer product.

7. The method of claim 6 wherein the protected hydroxyl moiety is selected from the group consisting of silyl ethers, silyl esters, acetate and mixtures thereof.

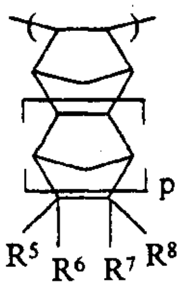
8. The method of claim 7 wherein the functional group containing the protected hydroxyl moiety is selected from the group consisting of $-(CH_2)_nOG$, $-(CH_2)_nC(O)OG$, and $-(CH_2)_n-(C_6$ to $C_{14})$aryl-OG′ wherein n is an integer from 0 to 10 and G is a silyl protecting group of the formula $-Si(R^{15})_3$ wherein R^{15} independently represents linear and branched (C_1 to C_{10}) alkyl, (C_6 to C_{14}) aryl, and substituted (C_6 to C_{14}) aryl wherein said substituents are selected form linear and branched (C_1 to C_5) alkyl groups; and G′represents G or $-C(O)CH_3$.

9. The method of claim 6 wherein the deprotected hydroxyl moiety is selected from the group consisting of an alcohol, carboxylic acid, and mixtures thereof.

10. The method of claim 9 wherein the deprotected group is an alcohol and said polymer is coreacted with a coreactive moiety selected from the group consisting of succinic anhydride, isocyanates of the formula R^{16}-NCO, sulfonate esters of the formula: $R^{16}-SO_2-O-SO_2-R^{16}$ and coreactive moieties of the formula $R^{16}-C(O)O(O)C-R^{16}$ wherein R^{16} independently represents a linear and branched (C_1 to C_{10}) alkyl group, (C_6 to C_{20}) aryl, (C_7 to C_{24}) aralkyl, or a silyl group represented by the formula $-(CH_2)_n-Si(R^{19})_3$, wherein R^{19} independently represents a linear or branched (C_1 to C_{10}) alkyl group, (C_6 to C_{20}) aryl, (C_7 to C_{24}) aralkyl, and n is an integer from 0 to 10.

11. The method of claim 9 wherein the deprotected group is carboxylic acid and said polymer is coreacted with a coreactive moiety selected from the group consisting of linear and branched acetals, cyclic acetals, orthocarbonates, vinyl ethers, and mixtures thereof.

12. A method for preparing a post-functionalized cyclic polymer comprising reacting a base polymer containing repeating units of the formula:



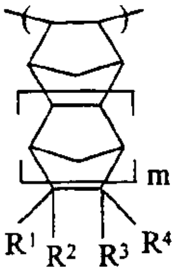
wherein p is an integer from 0 to 5; R^5 to R^8 independently represent hydrogen, linear and branched (C_1 to C_{20}) alkyl, $-(CH_2)_nC(O)OR$, $-(CH_2)_nOR$,

-$(CH_2)_nOC(O)R$, -$(CH_2)_nC(O)R$, -$(CH_2)_nOC(O)OR$, wherein R is linear or branched (C_1 to C_{10}) alkyl subject to the proviso that at least one of R^5 to R^8 is independently selected from a deprotected functional group represented by -$(CH_2)_nOH$, -$(CH_2)_nC(O)OH$, and -$(CH_2)_n$-(C_6 to C_{14})aryl-OH, wherein n is an integer from 0 to 10 with a moiety coreactive with said deprotected functional group.

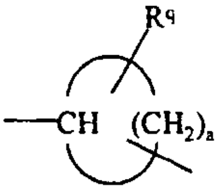
13. The method of claim 12 wherein said deprotected functional group is selected from the group consisting of -$(CH_2)_nOH$, -$(CH_2)_n$-(C_6 to C_{14})aryl-OH, and mixtures thereof and said coreactive moiety is selected from the group consisting of succinic anhydride, isocyanates of the formula R^{16}-NCO, sulfonate esters of the formula: R^{16}-SO_2-O-SO_2-R^{16} and coreactive moieties of the formula R^{16}-C(O)O(O)C-R^{16} wherein R^{16} independently represents a linear and branched (C_1 to C_{10}) alkyl group, (C_6 to C_{20}) aryl, (C_7 to C_{24}) aralkyl, or a silyl group represented by the formula -$(CH_2)_n$-$Si(R^{19})_3$, wherein R^{19} independently represents a linear or branched (C_1 to C_{10}) alkyl group, (C_6 to C_{20}) aryl, (C_7 to C_{24}) aralkyl, and n is an integer from 0 to 10.

14. The method of claim 12 wherein said deprotected functional group is -$(CH_2)_nC(O)OH$ and said coreactive moiety is selected from the group consisting of linear and branched acetals, cyclic acetals, orthocarbonates, vinyl ethers, and mixtures thereof.

15. The method of claim 12, 13, or 14 wherein said base polymer further comprises a repeating unit of the formula:



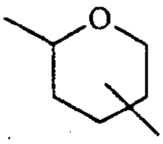
m is an interger from 0 to 10, wherein R^1 to R^4 independently represent a substituent selected from the group $-(A)_nC(O)OR*$, $-(A)_n-C(O)OR$, $-(A)_n-OR$, $-(A)_n-OC(O)R$, $-(A)_n-C(O)R$, $-(A)_n-OC(O)OR$, $-(A)_n-OCH_2C(O)OR*$, $-(A)_n-C(O)O-A'-OCH_2C(O)OR*$, $-(A)_n-OC(O)-A'-C(O)OR*$, $-(A)_n-C(R)_2CH(R)(C(O)OR**)$, and $-(A)_n-C(R)_2CH(C(O)OR**)_2$ subject to the proviso that at least one of R^1 to R^4 is selected from an acid labile group containing R^*; A and A′ independently represent a divalent bridging or spacer radical selected from divalent hydrocarbon radicals selected from linear and branched (C_1 to C_{10}) alkylene; divalent cyclic hydrocarbon radicals selected from substituted and unsubstituted (C_3 to C_8) cycloaliphatic moieties of the formula:



wherein "a" is an integer from 2 to 7 and R^q if present represents linear and branched (C_1 to C_{10}) alkyl groups: divalent oxygen containing radicals selected from (C_2 to C_{10}) alkylene ethers and polyethers of the formula:

$$-(CH_2(CH_2)_xO)_y-$$

wherein x is an integer from 1 to 5 and y is an integer from 2 to 50, with the proviso that the terminal oxygen atom on the polyether spacer moiety can not be directly linked to a terminal oxygen atom on an adjacent group to form a peroxide linkage; and divalent cyclic ethers and cyclic diethers represented by the structures:



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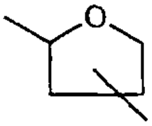

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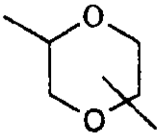
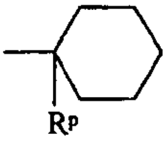


and R^* is acid labile group selected from Dcpm, Dmcp, $-C(CH_3)_3$, $-CH(R^p)OCH_2CH_3$, $-CH(R^p)OC(CH_3)_3$, and the cyclic group:



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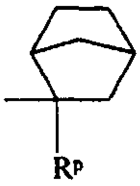

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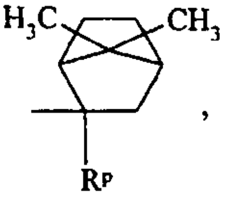

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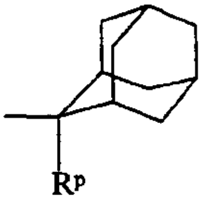

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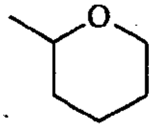

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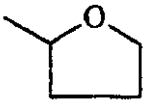

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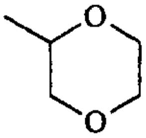
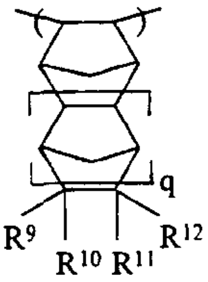
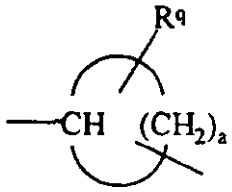


or mixtures thereof, wherein R^p represents hydrogen and a linear or branched (C_1 to C_5) alkyl group.

16. The method of claim 15 wherein said base polymer further comprises a repeating unit of the formula:



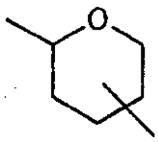
wherein q is an integer from 0 to 5; R^9 to R^{12} independently represent hydrogen, linear or branched (C_1 to C_{10}) alkyl, or a substituent selected from the group $-(A)_n-C(O)OR''$, $-(A)_n-OR''$, $-(A)_n-OC(O)R''$, $-(A)_n-OC(O)OR''$, $-(A)_n-C(O)R''$, $-(A)_n-OC(O)C(O)OR''$, $-(A)_n-O-A'-C(O)OR''$, $-(A)_n-OC(O)-A'-C(O)OR''$, $-(A)_n-C(O)O-A'-C(O)OR''$, $-(A)_n-C(O)-A'-OR''$, $-(A)_n-C(O)O-A'-OC(O)OR''$, $-(A)_n-C(O)O-A'-O-A'-C(O)OR''$, $-(A)_n-C(O)O-A'-OC(O)C(O)OR''$, $-(A)_n-C(R'')_2CH(R'')(C(O)OR'')$, and $-(A)_n-C(R'')_2CH(C(O)OR'')_2$, R^9 and R^{12} can be taken together with the ring carbon atoms to which they are attached to represent a cyclic anhydride group; A and A' independently represent a divalent bridging or spacer radical selected from divalent hydrocarbon radicals selected from linear and branched (C_1 to C_{10}) alkylene; divalent cyclic hydrocarbon radicals selected from substituted and unsubstituted (C_3 to C_8) cycloaliphatic moieties of the formula:



wherein "a" is an integer from 2 to 7 and R^q if present represents linear and branched (C_1 to C_{10}) alkyl groups; divalent oxygen containing radicals selected from (C_2 to C_{10}) alkylene ethers and polyethers of the formula:

$$-\!\left(CH_2(CH_2)_xO\right)_y\!-$$

wherein x is an integer from 1 to 5 and y is an integer from 2 to 50, with the proviso that the terminal oxygen atom on the polyether spacer moiety can not be directly linked to a terminal oxygen atom on an adjacent group to form a peroxide linkage; and divalent cyclic ethers and cyclic diethers represented by the structures:



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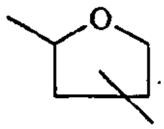

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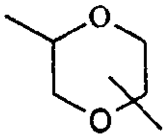

R″ independently represents, linear and branched (C_1 to C_{10}) alkyl, linear and branched (C_1 to C_{10}) alkoxyalkylene, polyethers, monocyclic and polycyclic (C_4 to C_{20}) cycloaliphatic moieties, cyclic ethers, cyclic ketones, and cyclic esters.

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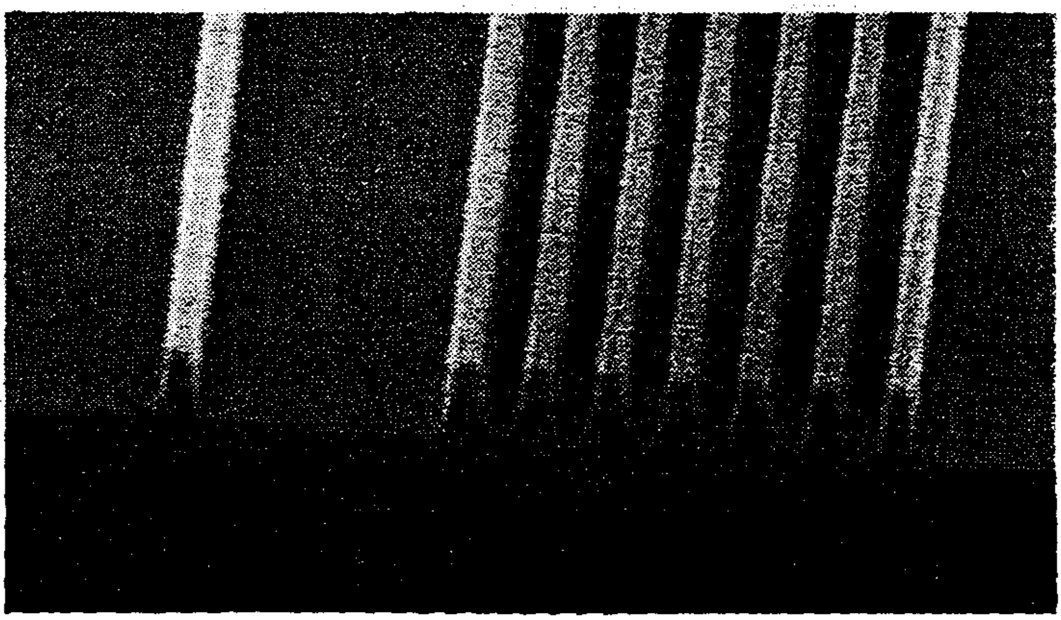

FIG-1

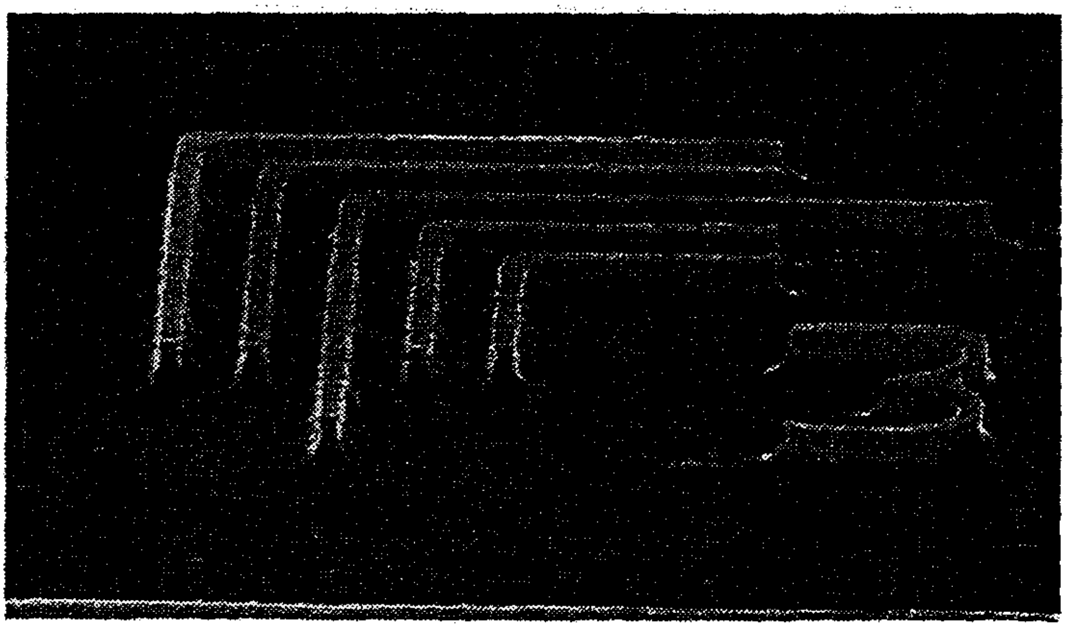

FIG-2

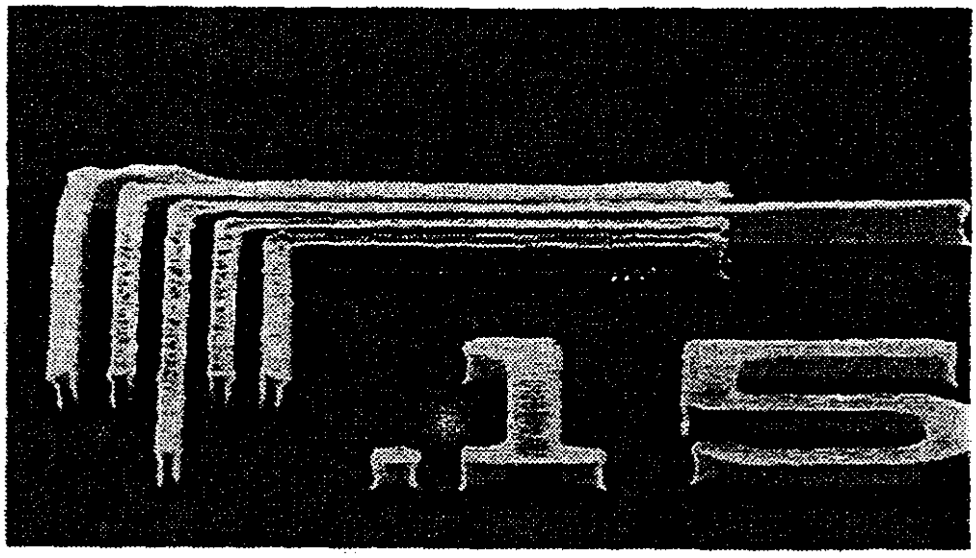

FIG-3

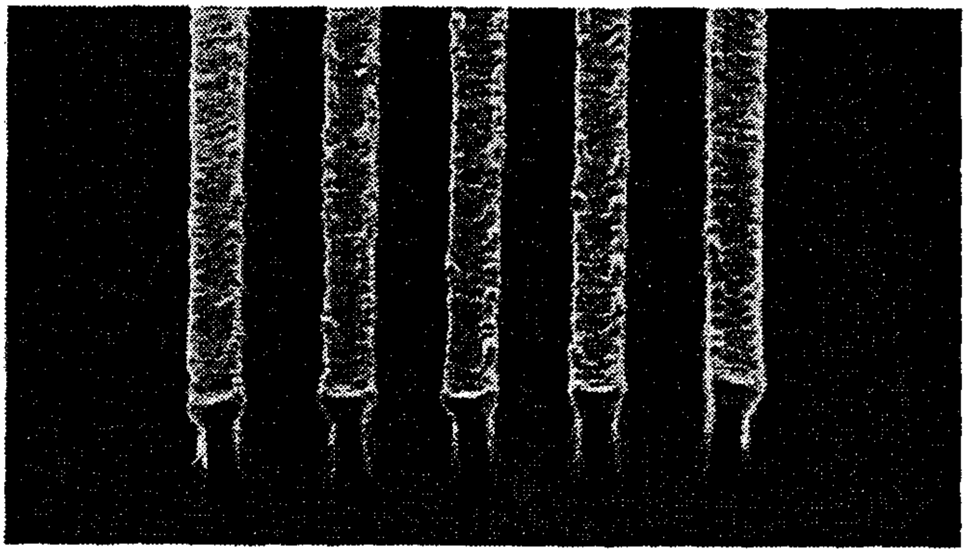

FIG-4

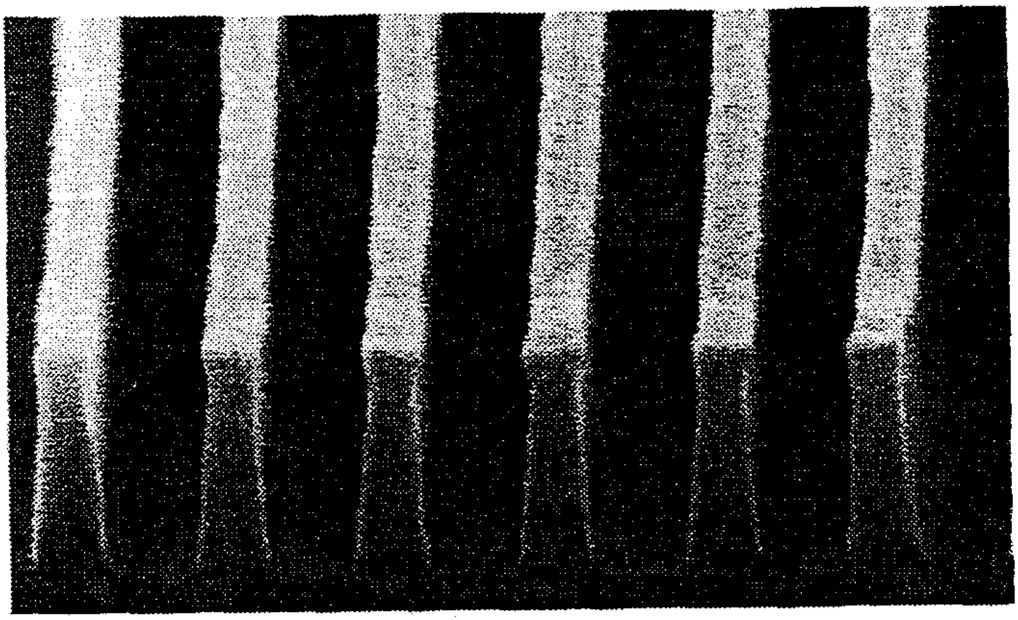

FIG-5

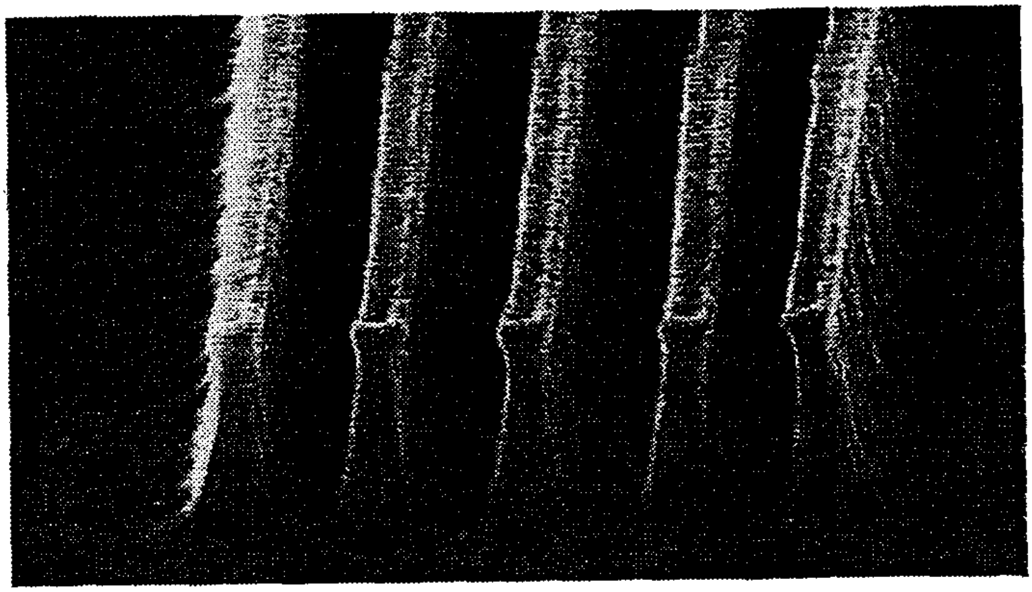

FIG-6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/03771

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G61/08 G03F7/038 G03F7/075

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G G03F

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 33198 A (GOODRICH CO B F) 12 September 1997	1
Y	see claims 1,2; example 10 ---	2
A	EP 0 789 278 A (JAPAN SYNTHETIC RUBBER CO LTD) 13 August 1997 ---	1
Y	PATENT ABSTRACTS OF JAPAN vol. 009, no. 182 (P-376), 27 July 1985 & JP 60 052845 A (NIPPON GOSEI GOMU KK), 26 March 1985 see abstract -----	2

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" *document which may throw doubts on priority claim(s) or* which is cited to establish the publication date of another citation or other special reason (as specified)

"O" *document referring* to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the *invention*

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to *involve an inventive step when the document is taken alone*

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 10 June 1999	Date of mailing of the international search report 21/06/1999
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, *Fax: (+31-70) 340-3016*	Authorized officer Devriese, K

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter...onal Application No
PCT/US 99/03771

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9733198 A	12-09-1997	AU 2327297 A	22-09-1997
		EP 0885405 A	23-12-1998
EP 0789278 A	13-08-1997	JP 10111569 A	28-04-1998

Form PCT/ISA/210 (patent family annex) (July 1992)

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G03F 7/038 G03F 7/075

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[85]进入国家阶段日期 2000.9.26
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R·D·艾伦 R·A·迪彼特罗
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代理人 刘金辉

权利要求书8页 说明书47页 附图页数3页

[54]发明名称 改性的多环聚合物

[57]摘要

本发明涉及环状聚合物和其在照相平版印刷应用中的用途。这些环状聚合物含有酸不稳定官能侧基和含保护的羟基部分的官能基团。这些聚合物通过使羟基侧基部分脱保护并使该含脱保护羟基的部分与共反应剂反应而进行后改性。发现这些后-官能化的聚合物可用于化学放大光刻胶组合物中。

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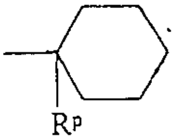
权利要求书

1. 一种含环状主链的聚合物，所述主链包括酸不稳定官能侧基和含被保护羟基部分的被保护官能基团。

2. 权利要求 1 的聚合物，其中所述酸不稳定官能侧基被含酸不稳定基团的酯部分封端，所述酸不稳定基团选自 Dcpm、Dmcp、$-C(CH_3)_3$、$-CH(R^p)OCH_2CH_3$、$CH(R^p)\ OC(CH_3)_3$ 和如下环状基团:



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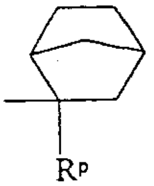

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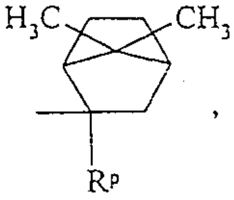

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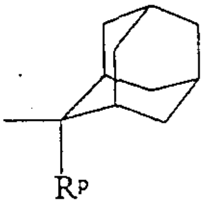

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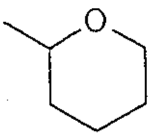

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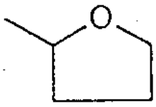

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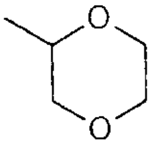
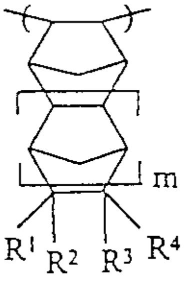


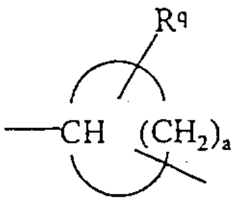
或其混合物，其中R^p表示氢和线性或支化$(C_1$至$C_5)$烷基；所述被保护官能基团含甲硅烷基保护的羟基部分。

3. 权利要求2的聚合物，其中所述被保护官能基团由通式$-(CH_2)_nOG$、$-(CH_2)_nC(O)OG'$和$-(CH_2)_n-(C_6$至$C_{14})$芳基$-OG$的基团表示，其中n为0至10的整数，G为通式$-Si(R^{15})_3$的甲硅烷基保护基团，其中R^{15}独立地表示线性和支化$(C_1$至$C_{10})$烷基、$(C_6$至$C_{14})$芳基和取代的$(C_6$至$C_{14})$芳基，其中所述取代基选自线性和支化$(C_1$至$C_5)$烷基；和G'表示G或$-C(O)CH_3$。

4. 一种包括环状重复单元的聚合物，其中所述重复单元的一部分含酸不稳定侧基，所述重复单元的另一部分含被保护官能侧基，所述含酸不稳定侧基的重复单元由如下结构表示:



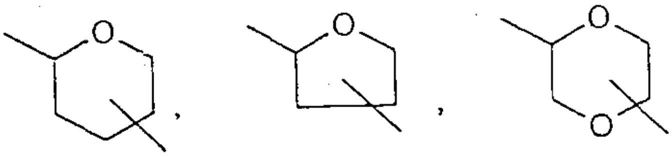
m 为 0 至 10 的整数，其中 R^1 至 R^4 独立地表示选自基团 $-(A)_nC(O)OR^*$，$-(A)_n-C(O)OR$，$-(A)_n-OR$，$-(A)_n-OC(O)R$，$-(A)_n-C(O)R$，$-(A)_n-OC(O)OR$，$-(A)_n-OCH_2C(O)OR^*$，$-(A)_n-C(O)O-A'-OCH_2C(O)OR^*$，$-(A)_n-OC(O)-A'-C(O)OR^*$，$-(A)_n-C(R)_2CH(R)(C(O)OR^{**})$ 和 $-(A)_n-C(R)_2CH(C(O)OR^{**})_2$ 的取代基，条件是 R^1 至 R^4 中至少一个选自含 R^* 的酸不稳定基团，A 和 A′ 独立地表示选自如下的二价桥连或间隔基团：选自线性和支化（C_1 至 C_{10}）亚烷基的二价烃基；选自如下通式表示的取代和未取代（C_3 至 C_8）环脂族部分的二价环烃基：



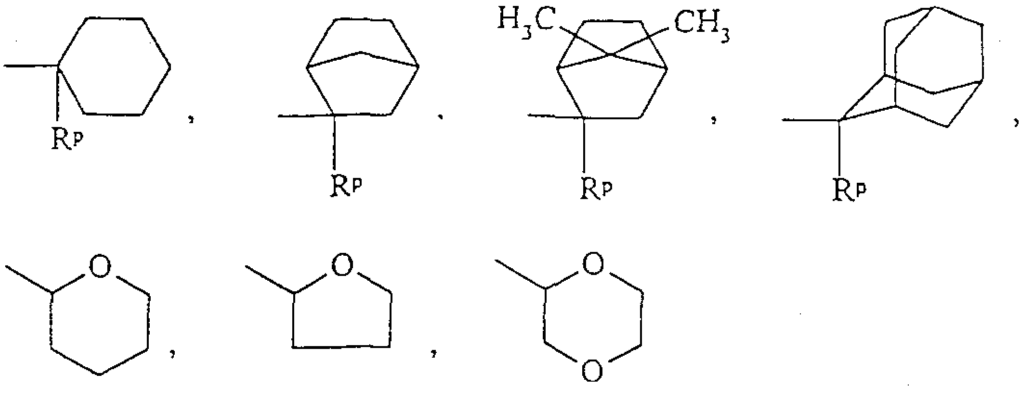
其中"a"为 2 至 7 的整数，和 R^q 当存在时表示线性和支化（C_1 至 C_{10}）烷；选自（C_2 至 C_{10}）亚烷基醚和如下通式的聚醚的二价含氧基团：

$$-(CH_2(CH_2)_xO)_y-$$

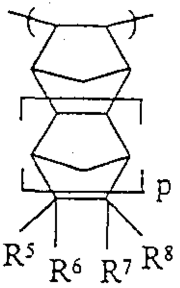
其中 x 为 1 至 5 的整数，y 为 2 至 50 的整数，条件是聚醚间隔部分上的末端氧原子不能与相邻基团上的末端氧原子直接连接形成过氧化物链；和如下结构表示的二价环状醚和环状二醚：



其中 R^* 为选自 Dcpm、Dmcp、$-C(CH_3)_3$、$-CH(R^p)OCH_2CH_3$、$-CH(R^p)OC(CH_3)_3$ 和如下环状基团：

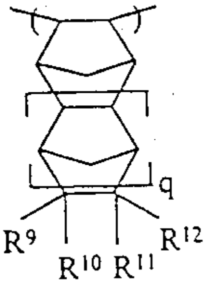


或其混合物的酸不稳定基团，其中R^p表示氢和线性或支化(C_1至C_5)烷基；所述含被保护官能基团的重复单元由如下结构表示：



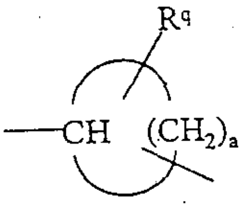
其中p为0至5的整数；R^5至R^8独立地表示氢、线性和支化(C_1至C_{20})烷基、$-(CH_2)_nC(O)OR$、$-(CH_2)_nOR$、$-(CH_2)_nOC(O)R$、$-(CH_2)_nC(O)R$、$-(CH_2)_nOC(O)OR$，其中R为线性或支化(C_1至C_{10})烷基，条件是R^5至R^8中至少一个选自由$-(CH_2)_nOG$、$-(CH_2)_nC(O)OG$和$-(CH_2)_n-(C_6$至$C_{14})$芳基$-OG'$表示的被保护官能基团，其中n为0至10的整数，G为选自基团$-Si(R^{15})_3$的保护基团，其中R^{15}独立地表示线性和支化(C_1至C_{10})烷基、(C_6至C_{14})芳基、取代(C_6至C_{14})芳基，其中所述取代基选自线性和支化(C_1至C_5)烷基，G'表G或$-C(O)CH_3$。

5. 权利要求4的聚合物，还包括如下结构表示的重复单元：



其中q为0至5的整数；R^9至R^{12}独立地表示氢、线性或支化(C_1至C_{10})烷基，或选自如下基团的取代基：$-(A)_n-C(O)OR''$，$-(A)_n-OR''$，$-(A)_n-OC(O)R''$，$-(A)_n-OC(O)OR''$，$-(A)_n-C(O)R''$，$-(A)_n-OC(O)C(O)OR''$，$-(A)_n-O-A'-C(O)OR''$，$-(A)_n-OC(O)-A'-C(O)OR''$，$-(A)_n-C(O)O-A'-C(O)OR''$，$-(A)_n-C(O)-A'-OR''$，$-(A)_n-C(O)O-A'-OC(O)OR''$，$-(A)_n-C(O)O-A'-O-A'-C(O)OR''$，$-(A)_n-C(O)O-A'-OC(O)C(O)OR''$，$-(A)_n-C(R'')_2CH(R'')(C(O)OR'')$和$-(A)_n-C(R'')_2CH(C(O)OR'')_2$；$R^9$和$R^{12}$可与连

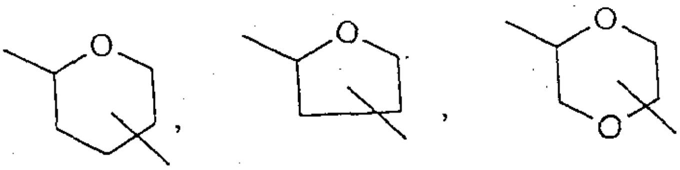
接它们的环碳原子一起表示环状酸酐基团；A 和 A′独立地表示选自如下的二价桥连或间隔基团：选自线性和支化(C_1 至 C_{10})亚烷基的二价烃基；选自如下通式表示的取代和未取代(C_3 至 C_8) 环脂族部分的二价环烃基：



其中“a”为 2 至 7 的整数，和 R^q 当存在时表示线性和支化(C_1 至 C_{10})烷；选自(C_2 至 C_{10})亚烷基醚和如下通式的聚醚的二价含氧基团：

$$-(CH_2(CH_2)_xO)_y-$$

其中 x 为 1 至 5 的整数，y 为 2 至 50 的整数，条件是聚醚间隔部分上的末端氧原子不与相邻基团上的末端氧原子直接连接形成过氧化物键；和如下结构表示的二价环状醚和环状二醚：



R″独立地表示线性和支化(C_1 至 C_{10}) 烷基、线性和支化(C_1 至 C_{10})烷氧基亚烷基、聚醚、单环和多环(C_4 至 C_{20})环脂族部分、环醚、环酮和环酯。

6. 一种后官能化含环状重复单元的聚合物的方法，包括如下步骤：
a)提供包括含酸不稳定官能侧基的环状重复单元和含有含被保护羟基部分的官能侧基的环状重复单元的基础聚合物；
b)使被保护羟基部分脱保护得到含游离羟基的官能基团；
c)将游离羟基与共反应部分反应得到后官能化的聚合物产物。

7. 权利要求 6 的方法，其中被保护羟基部分选自甲硅烷基醚、甲硅烷基酯、乙酸酯和其混合物。

8. 权利要求7的方法，其中含被保护羟基部分的官能基团选自$-(CH_2)_nOG$、$-(CH_2)_nC(O)OG$和$-(CH_2)_n-(C_6$至$C_{14})$芳基$-OG'$，其中n为0至10的整数，G为式$-Si(R^{15})_3$的甲硅烷基保护基团，其中R^{15}独立地表示线性

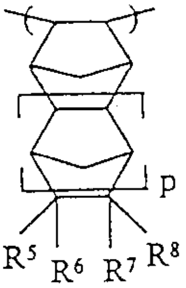
和支化(C_1至C_{10})烷基、(C_6至C_{14})芳基、取代(C_6至C_{14})芳基，其中所述取代基选自线性和支化(C_1至C_5)烷基，G′表G或$-C(O)CH_3$。

9. 权利要求6的方法，其中脱保护的羟基部分选自醇、羧酸和其混合物。

10. 权利要求9的方法，其中脱保护基团为醇，所述聚合物与选自琥珀酸酐，通式$R^{16}-NCO$的异氰酸酯、通式$R^{16}-SO_2-O-SO_2-R^{16}$的磺酸酯和通式$R^{16}-C(O)O(O)C-R^{16}$的共反应部分的共反应部分共反应，其中$R^{16}$独立地表示线性或支化($C_1$至$C_{10}$)烷基、($C_6$至$C_{20}$)芳基、($C_7$至$C_{24}$)芳烷基，或通式$-(CH_2)_n-Si(R^{19})_3$表示的甲硅烷基，其中$R^{19}$独立地表示线性或支化($C_1$至$C_{10}$)烷基、($C_6$至$C_{20}$)芳基、($C_7$至$C_{24}$)芳烷基，n为0至10的整数。

11. 权利要求 9 的方法，其中脱保护基团为羧酸且所述聚合物与选自线性和支化缩醛、环状缩醛、原碳酸酯、乙烯基醚和其混合物的共反应部分共反应。

12. 一种制备后官能化的环状聚合物的方法，包括将含如下通式的重复单元的基础聚合物与可和所述脱保护官能团共反应的部分反应：



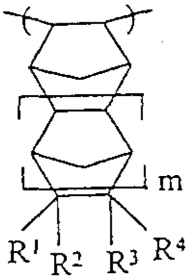
其中p为0至5的整数；R^5至R^8独立地表示氢、线性和支化(C_1至C_{20})烷基、$-(CH_2)_nC(O)OR$、$-(CH_2)_nOR$、$-(CH_2)_nOC(O)R$、$-(CH_2)_nC(O)R$、$-(CH_2)_nOC(O)OR$，其中R为线性或支化(C_1至C_{10})烷基，条件是R^5至R^8中至少一个独立地选自由$-(CH_2)_nOH$、$-(CH_2)_nC(O)OH$和$-(CH_2)_n-$(C_6至C_{14})芳基-OH表示的脱保护官能基团，其中n为0至10的整数。

13. 权利要求12的方法，其中所述脱保护官能基团选自$-(CH_2)_nOH$、$-(CH_2)_n-$(C_6至C_{14})芳基-OH和其混合物，所述共反应部分选自琥珀酸酐，通式$R^{16}-NCO$的异氰酸酯、通式$R^{16}-SO_2-O-SO_2-R^{16}$的磺酸酯和通式$R^{16}-C(O)O(O)C-R^{16}$的共反应部分，其中$R^{16}$独立地表示线性或支化($C_1$至$C_{10}$)

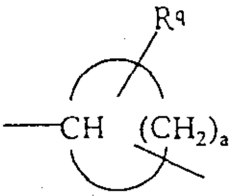
烷基、(C_6至C_{20})芳基、(C_7至C_{24})芳烷基，或通式$-(CH_2)_n-Si(R^{19})_3$表示的甲硅烷基，其中R^{19}独立地表示线性或支化(C_1至C_{10})烷基、(C_6至C_{20})芳基、(C_7至C_{24})芳烷基，n为0至10的整数。

14. 权利要求12的方法，其中所述脱保护官能基团为$-(CH_2)_nC(O)OH$，所述共反应部分选自线性和支化缩醛、环状缩醛、原碳酸酯、乙烯基醚和其混合物。

15. 权利要求12、13或14的方法，其中所述基础聚合物还包括如下通式的重复单元：



m为0至10的整数，其中R^1至R^4独立地表示选自$-(A)_nC(O)OR^*$，$-(A)_n-C(O)OR$，$-(A)_n-OR$，$-(A)_n-OC(O)R$，$-(A)_n-C(O)R$，$-(A)_n-OC(O)OR$，$-(A)_n-OCH_2C(O)OR^*$，$-(A)_n-C(O)O-A'-OCH_2C(O)OR^*$，$-(A)_n-OC(O)-A'-C(O)OR^*$，$-(A)_n-C(R)_2CH(R)(C(O)OR^{**})$和$-(A)_n-C(R)_2CH(C(O)OR^{**})_2$的基团，条件是$R^1$至$R^4$中至少一个选自含$R^*$的酸不稳定基团，A和A'独立地表示选自如下的二价桥连或间隔基团：选自线性和支化(C_1至C_{10})亚烷基的二价烃基；选自如下通式表示的取代和未取代(C_3至C_8)环脂族部分的二价环烃基：

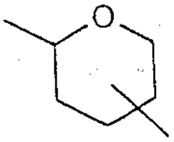


其中"a"为2至7的整数，和R^q当存在时表示线性和支化(C_1至C_{10})烷；选自(C_2至C_{10})亚烷基醚和如下通式的聚醚的二价含氧基团：

$$-(CH_2(CH_2)_xO)_y-$$

其中x为1至5的整数，y为2至50的整数，条件是聚醚间隔部分上

的末端氧原子不与相邻基团上的末端氧原子直接连接形成过氧化物键；和如下结构表示的二价环状醚和环状二醚: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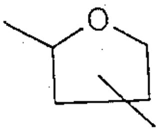
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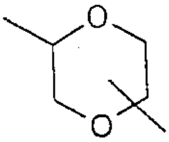
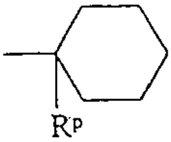


R^*表示选自 Dcpm、Dmcp、$-C(CH_3)_3$、$-CH(R^p)OCH_2CH_3$、$-CH(R^p)OC(CH_3)_3$ 或下列环状基团: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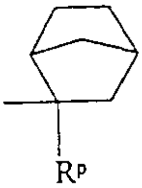
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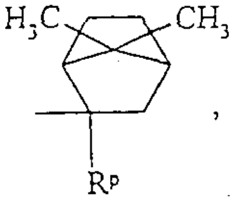
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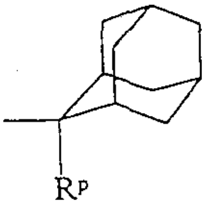
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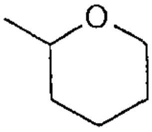
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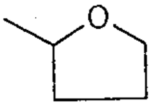
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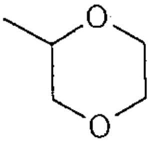
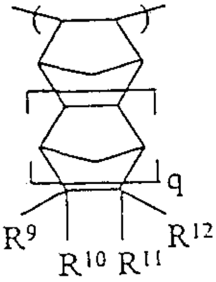


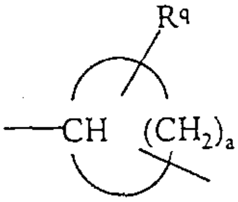
或其混合物的酸不稳定基团，其中 R^p 表示氢或线性或支化 (C_1 至 C_5) 烷基。

16. 权利要求 15 的方法，其中所述基础聚合物还包括如下通式的重复单元:



其中 q 为 0 至 5 的整数；R^9 至 R^{12} 独立地表示氢、线性或支化 (C_1 至 C_{10}) 烷基，或选自如下基团的取代基: $-(A)_n-C(O)OR''$，$-(A)_n-OR''$，$-(A)_n-OC(O)R''$，$-(A)_n-OC(O)OR''$，$-(A)_n-C(O)R''$，$-(A)_n-OC(O)C(O)OR''$，$-(A)_n-O-A'-C(O)OR''$，$-(A)_n-OC(O)-A'-C(O)OR''$，$-(A)_n-C(O)O-A'-C(O)OR''$，$-(A)_n-C(O)-A'-OR''$，$-(A)_n-C(O)O-A'-OC(O)OR''$，$-(A)_n-C(O)O-A'-O-A'-C(O)OR''$，$-(A)_n-C(O)O-A'-OC(O)C(O)OR''$，$-(A)_n-C(R'')_2CH(R'')(C(O)OR'')$ 和 $-(A)_n-C(R'')_2CH(C(O)OR'')_2$； R^9 和 R^{12} 可与

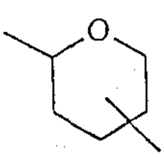
连接它们的环碳原子一起表示环状酸酐基团；A 和 A′独立地表示选自如下的二价桥连或间隔基团：选自线性和支化 $(C_1$ 至 $C_{10})$ 亚烷基的二价烃基；选自如下通式表示的取代和未取代 $(C_3$ 至 $C_8)$ 环脂族部分的二价环烃基：



其中“a”为 2 至 7 的整数，和 R^q 当存在时表示线性和支化 $(C_1$ 至 $C_{10})$ 烷；选自 $(C_2$ 至 $C_{10})$ 亚烷基醚和如下通式的聚醚的二价含氧基团：

$$-(CH_2(CH_2)_xO)_y-$$

其中 x 为 1 至 5 的整数，y 为 2 至 50 的整数，条件是聚醚间隔部分上的末端氧原子不与相邻基团上的末端氧原子直接连接形成过氧化物键；和如下结构表示的二价环状醚和环状二醚：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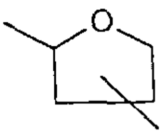
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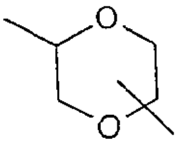


R″独立地表示线性和支化 $(C_1$ 至 $C_{10})$ 烷基、线性和支化 $(C_1$ 至 $C_{10})$ 烷氧基亚烷基、聚醚、单环和多环 $(C_4$ 至 $C_{20})$ 环脂族部分、环醚、环酮和环酯。

说　明　书

改性的多环聚合物

本发明背景

1. 技术领域

本发明涉及多环聚合物和其在照相平版印刷应用中的使用方法。本发明更具体涉及改性含官能侧基的多环聚合物和其在制造集成电路(IC)的光刻胶组合物中的用途。

2. 背景

当今电子工业的趋势是日益需要更快且消耗较低能量的 IC。为满足这些要求，IC 必须是具有亚微米特征尺寸的高密度的。导线必须做得更细且排列更近。降低导线之间的间隔导致 IC 的效率同时提高，使储存容量更大且信息在计算机芯片上的加工速度更快。为获得更薄的线宽和更小的特征尺寸，需要更高的图形分辨率。

IC 的图形形成通过本领域已知的各种平版印刷工艺进行。采用紫外(UV)光和渐深 UV 光或其它辐射的照相平板印刷是生产 IC 器件中使用的基本且重要的工艺。将感光聚合物膜（光刻胶）涂于基材表面(如薄片）并干燥。然后将包含所需图形信息的光掩模紧靠光刻胶膜放置。用包括 UV 光、电子束、x-射线或离子束的各种成像辐射之一经上面的光掩模照射光刻胶。在照射下曝光时，光刻胶发生化学变化并使溶解性改变。照射后，将基材浸入显影溶液中，使感光聚合物薄膜中的成像图形显影（即选择性除去曝光或未曝光区域）。根据所用光刻胶的类型或显影溶剂的极性，在显影过程中除去薄膜曝光或未曝光的区域，使下面的基材曝光，然后通过刻蚀方法除去或改变曝光的图形或不需要的基材物质，将所需的图形留在薄片的功能层上。余下的光刻胶物质起到阻止刻蚀的保护阻挡层的作用。除去余下的光刻胶物质即得图形化电路。刻蚀通等离子体刻蚀、溅射刻蚀和活性离子刻蚀(RIE)完成。

刻蚀通常包括将气体通入室中并在该气体存在下通过在两电极之间施加电压使气体电离。使用含有通过电压产生的离子物质的等离子体来刻蚀置于室中的基材。这些在等离子体中生成的离子物质作用于具有图形的基材上使其与表面物质相互作用形成可从表面除去的挥发性物质。活性离子刻蚀在基材中提供更好限定的垂直侧壁轮廓并使基材与基材之间的刻蚀更均匀。由于这些优点，活性离子刻蚀工艺在 IC 制造中已变成一种标准方法。

在制造高密度 IC 中，光刻胶膜的涂敷、曝光和显影是非常重要的。重要的是要控制成像和显影光刻胶的线宽接近容忍度。图形化光刻胶结构的轮廓必须与垂直侧壁笔直。此外，图形化抗蚀剂必须耐受随后的 IC 加工步骤，如 RIE。要求这些高性能聚合物抗蚀剂具有各种聚合物性能如亲水性、粘结性、照射曝光与未曝光区域之间的不同溶解性（即良好的分辨率和对比度性能）和耐 RIE 性能的优异平衡性。因此，化学放大抗蚀组合物在制造这些高密度 IC 器件中越来越流行。

Ito 等人的 US4,491,628 公开了一种含感光酸生成剂和聚合物组分的化学放大光刻胶组合物，所述聚合物组分具有酸不稳定侧基，包括羧酸的叔丁基酯和苯酚的叔丁基碳酸酯侧基。

Allen 等人的 US5,372,912 公开一种包括丙烯酸酯基共聚物、酚醛粘结剂和感光酸生成剂的化学放大光刻胶组合物。该共聚物组分包括丙烯酸或甲基丙烯酸、丙烯酸或甲基丙烯酸的烷基酯和具有酸不稳定侧基如羧酸的叔丁基酯和苯酚的叔丁基碳酸酯侧基的单体的反应产物。可通过改变公开的单体的含量调节该共聚物的性能。

The B.F. Goodrich Company 的国际专利申请 WO 97/33198 公开了一种化学放大光刻胶组合物，包括含具有酸不稳定侧基的重复单元的多环聚合物。此外，该聚合物可包括具有各种中性基团、酸基、烷基或其混合物侧基的多环重复单元。这些多环聚合物对短波长成像照射显示良好的透明性，同时能够承受 RIE 加工工艺。此外，可使用官能基团的宽变化可使本领域熟练技术人员在宽的应用范围内调节聚合物的性能。聚合物上的酸不稳定基团开裂使聚合物具有极性或溶解性，

而中性基团使聚合物具有亲水性或溶解性，促进润湿并改进薄膜的性能。酸基侧基使聚合物具有亲水性/润湿性，并使聚合物具有粘结性。烷基取代侧基可用于改变聚合物体系的 Tg。

尽管上述多环聚合物通过使用选取的官能侧基显示调节适用于高性能光刻胶的性能的灵活性，但存在的缺点在于含这些官能团中某些的环烯烃单体难以有效直接聚合。例如，含羟基（例如醇、羧酸、苯酚）和氮（例如酰胺、腈）的官能团可能抑制用于聚合这些官能环烯烃单体的催化剂体系，导致降低所需聚合物的收率。此外，具有某些官能团的环烯烃单体难以通过常规合成路线合成和纯化或并非总是能市购到。因此，需要另一在技术上可行、有效且经济的合成具有官能侧基的光刻胶聚合物的路线。

本发明概述

本发明的总目的是提供官能化可用于光刻胶组合物的聚合物的另一方法。

本发明的另一目的是后官能化包括多环重复单元的聚合物。

本发明的第三个目的是后官能化包括含酸不稳定侧基部分的重复单元的多环聚合物。

本发明的第四个目的是提供另一官能化具有含羟基、氮和硫的基团的多环聚合物的方法。

本发明的第五个目的是将含羧酸的部分通过后官能化反应引入多环聚合物主链中。

本发明的第六个目的是提供亲水性增加的光刻胶聚合物。

已发现，本发明的上述目的可通过由后官能化方法将难以聚合的官能团引入聚合物中制备适用于光刻胶组合物的多环聚合物的方法实现，该后官能化方法包括(a)提供包括含酸不稳定侧基的重复单元和含保护的羟基侧基部分的重复单元的多环基础聚合物组合物；(b)使含羟基部分脱保护得到游离羟基；和(c)将游离羟基与共反应部分反应得到后官能化部分。

附图的简要描述

图 1 为印刷于 50/50 草酸酯/叔丁基酯抗蚀聚合物上的图象在 0.30 μm 特征分辨率下的 SEM 显微照片。

图 2 为印刷于本发明含 10 mol%具有羧酸官能侧基的重复单元的抗蚀聚合物上的图象在 0.30 μm 特征分辨率下的 SEM 显微照片。

图 3 为印刷于本发明含 10 mol%具有羧酸官能侧基的重复单元的抗蚀聚合物上的图象在 0.15 μm 特征分辨率和 1:1 间距(pitch)下的 SEM 显微照片。

图 4 为印刷于本发明含 10 mol%具有羧酸官能侧基的重复单元的抗蚀聚合物上的图象在 0.12μm 特征分辨率和 2:1 间距下的 SEM 显微照片。

图 5 为印刷于本发明含 20 mol%具有羧酸官能侧基的重复单元的抗蚀聚合物上的图象在 0.16μm 特征分辨率和 1:1 间距下的 SEM 显微照片。

图 6 为印刷于本发明含 20 mol%具有羧酸官能侧基的重复单元的抗蚀聚合物上的图象在 0.10μm 特征分辨率和 3:1 间距下的 SEM 显微照片。

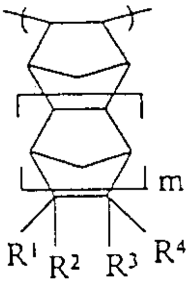
本发明详细描述

本发明涉及直接将官能基团引入包括含酸不稳定侧基的多环重复单元和含具有保护羟基的侧基部分的多环重复单元的基础聚合物中的方法。已发现该后官能化的聚合物可用于化学放大光刻胶组合物中。本发明方法适用于其中所需官能团不能通过直接聚合含所需官能团的单体引入聚合物中的情况。

本发明一方面中，将包括下述通式 I 和 II 的多环重复单元的基础聚合物后官能化，得到适用于化学放大光刻胶应用的聚合物。通式 I 的重复单元含酸不稳定侧基，通式 II 的重复单元包括含被保护羟基的侧基部分。此外，该基础聚合物组合物可非必要地含如下通式 III 的多环重复单元。本发明的基础聚合物通过含被保护羟基的侧基部分进

行后官能化。

本发明的含酸不稳定重复单元由如下通式 I 表示：

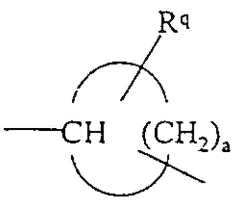


I

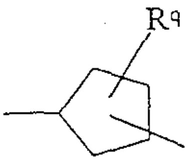
其中 R^1 至 R^4 独立地表示选自$-(A)_nC(O)OR^*$，$-(A)_n-C(O)OR$，$-(A)_n-OR$，$-(A)_n-OC(O)R$，$-(A)_n-C(O)R$，$-(A)_n-OC(O)OR$，$-(A)_n-OCH_2C(O)OR^*$，$-(A)_n-C(O)O-A'-OCH_2C(O)OR^*$，$-(A)_n-OC(O)-A'-C(O)OR^*$，$-(A)_n-C(R)_2CH(R)(C(O)OR^{**})$和$-(A)_n-C(R)_2CH(C(O)OR^{**})_2$ 的基团，条件是 R^1 至 R^4 中至少一个选自含 R^*的酸不稳定基团，优选$-(A)_nC(O)OR^*$。

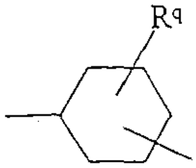
A 和 A'独立地表示选自二价烃基、二价环烃基、二价含氧基团以及二价环醚和环二醚的二价桥连或间隔基团，m 为 0 至 10 的整数，优选 0 或 1；n 为 0 或 1 的整数。当 n 为 0 时，显然 A 表示单共价键。术语二价是指在基团各末端处的自由价与两个不同基团连接。该二价烃基可由通式$-(C_dH_{2d})-$表示，其中 d 表示亚烷基链中的碳原子数并为 1 至 10 的整数。该二价烃基优选选自线性和支化(C_1 至 C_{10})亚烷基如亚甲基、亚乙基、亚丙基、亚丁基、亚戊基、亚己基、亚庚基、亚辛基、亚壬基和亚癸基。当为支化亚烷基时，应理解线性亚烷基链中的氢原子被线性或支化(C_1 至 C_5)烷基取代。

二价环烃基包括如下通式表示的取代和未取代(C_3 至 C_8) 环脂族部分：



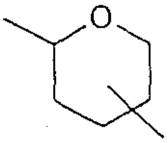
其中 a 为 2 至 7 的整数和 R^q(当存在时)表示线性和支化(C_1 至 C_{10})烷基。优选的二价环亚烷基包括如下结构表示的环亚戊基和环亚己基部分：

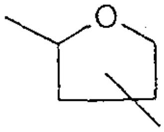


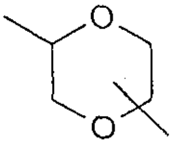
,


其中 R^q 为上面定义的。应注意，作为这里的说明和在整个说明书中，从环状结构和/或通式中伸出的两个键线表示该部分的二价特性，并表示环碳原子与相应通式中定义的相邻分子部分键合的点。正如本领域公知的，自环状结构中心伸出的斜键线表示该键非必要地与环中任一环碳原子连接。还应注意该键线连接的环碳原子将提供的氢原子要少一个以满足碳的价态要求。

优选的二价环状醚和二醚由如下结构表示：



,


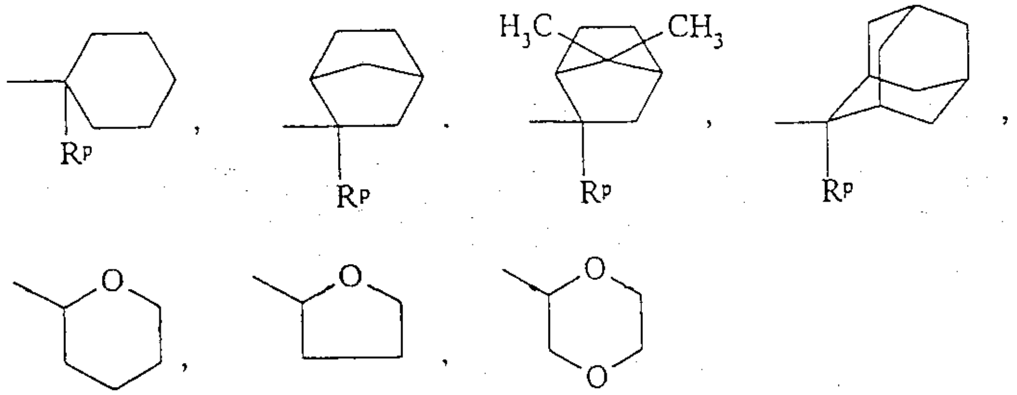
,


该二价含氧基团包括(C_2 至 C_{10})亚烷基醚和聚醚。(C_2 至 C_{10})亚烷基醚是指二价醚部分中的碳原子总数必须至少为 2 并不可超过 10。二价亚烷基醚由通式-亚烷基-O-亚烷基-表示，其中与氧原子键合的各亚烷基可以相同或不同，并选自亚甲基、亚乙基、亚丙基、亚丁基、亚戊基、亚己基、亚庚基、亚辛基和亚壬基。这一系列中最简单的二价亚烷基醚为基团$-CH_2-O-CH_2-$。优选的聚醚部分包括如下通式的二价基团：

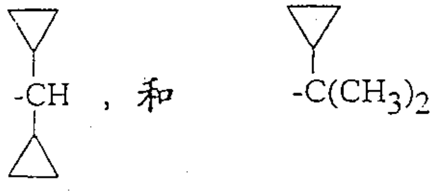
$$-(CH_2(CH_2)_xO)_y-$$

其中 x 为 1 至 5 的整数，y 为 2 至 50 的整数，条件是聚醚间隔部分上的末端氧原子不与相邻基团上的末端氧原子直接连接形成过氧化物键。换言之，当聚醚间隔基与上面 R^1 至 R^4 中所列的任一含末端氧取代基连接时，不考虑过氧化物键(即-O-O-)。

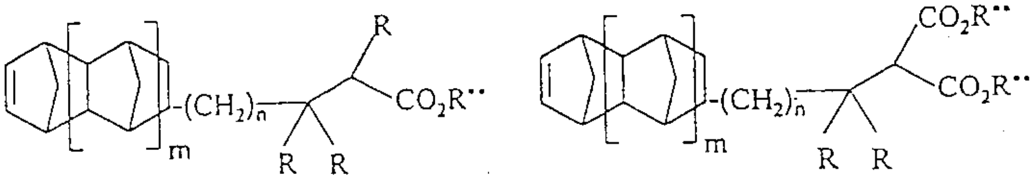
在上面的通式中 R 表示线性和支化(C_1 至 C_{10}) 烷基，R^*表示选自$-C(CH_3)_3$、$-CH(R^p)OCH_2CH_3$、$-CH(R^p)OC(CH_3)_3$ 或下列环状结构的可通过光致酸（photoacid）引发剂开裂的部分（即酸不稳定的封闭或保护基团）：



R^p表示氢或线性或支化(C_1至C_5)烷基。该烷基取代基包括甲基、乙基、丙基、异丙基、丁基、异丁基、叔丁基、戊基、叔戊基和新戊基。在上面的结构中，自环状基团伸出的单键线表示碳原子环位置，在该位置上保护基团与相应的取代基键合。酸不稳定基团的例子包括1-甲基-1-环己基、异冰片基、2-甲基-2-异冰片基、2-甲基-2-金刚烷基、四氢呋喃基、四氢吡喃基、3-氧代环己酮基、甲羟戊酸内酯基、1-乙氧基乙基、1-叔丁氧基乙基、二环丙基甲基(Dcpm)，和二甲基环丙基甲基(Dmcp)基团。R^{**}独立地表示上面定义的R和R^*。该Dcpm和Dmcp基团分别由如下结构表示：



具有选自基团$-(CH_2)_nC(R)_2CH(R)(C(O)OR^{**})$或$-(CH_2)_nC(R)_2CH(C(O)OR^{**})_2$的取代基的上述通式的多环单体可表示如下：

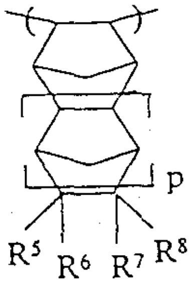


其中m为上面定义的，n为0至10的整数。

对本领域熟练技术人员而言显而易见的是，任何光致酸可开裂部分都适合实施本发明，只要聚合反应基本上不受此抑制即可。

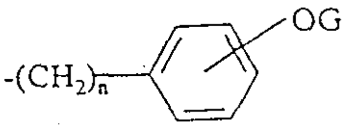
优选的酸不稳定基团为保护的有机酯基团，其中保护或封闭基团在酸存在下进行开裂反应。羧酸的叔丁基酯是特别优选的。

下面通式 II 表示的重复单元包括含保护的羟基部分的侧基。羟基部分是指含羟基的任何官能团。为简化起见，保护的部分还可称为保护的氧基。术语保护的氧基是指免受不期望的反应的氧原子。含羟基官能团的代表性例子包括醇、羧酸和酚。术语保护的羟基部分是指羟基部分中氧原子上的氢原子被保护基团暂时取代。该保护基团起到使官能基团免受不期望的副反应的作用，或阻止与其它官能团或聚合基础聚合物所用催化剂的不期望的反应。含保护的羟基的侧基部分的重复单元由如下通式表示：



II

其中 R^5 至 R^8 独立地表示氢、线性和支化 (C_1 至 C_{20}) 烷基、$-(CH_2)_nC(O)OR$、$-(CH_2)_nOR$、$-(CH_2)_nOC(O)R$、$-(CH_2)_nC(O)R$、$-(CH_2)_nOC(O)OR$，其中 R 为线性或支化 (C_1 至 C_{10}) 烷基。R^5 至 R^8 中至少一个选自 $-(CH_2)_nOG$、$-(CH_2)_nC(O)OG$ 和 $-(CH_2)_n-(C_6$ 至 $C_{14})$ 芳基 $-OG$ 表示的被保护基团。代表性芳基为苯基，萘基和蒽基。当芳基为苯基时，这些羟基被保护的取代基可表示如下：



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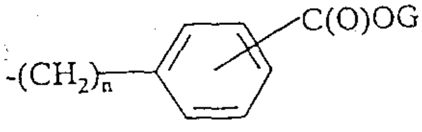
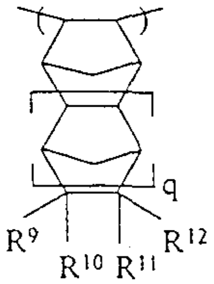


其中 n 为 0 至 10，优选 0 至 5 的整数；p 为 0 至 5，优选 0 或 1 的整数；G 为选自通式 $-Si(R^{15})_3$ 的取代基的保护基团，其中 R^{15} 独立地表示线性和支化 (C_1 至 C_{10}) 烷基、芳基如苯基、芳烷基如被线性或支化 (C_1 至 C_5) 烷基取代的苯基。代表性的甲硅烷基包括三甲基甲硅烷基、三乙基甲硅烷基、三异丙基甲硅烷基、二甲基异丙基甲硅烷基、二乙基异

丙基甲硅烷基、二甲基己基甲硅烷基、二甲基苯基甲硅烷基、叔丁基二甲基甲硅烷基、叔丁基二苯基甲硅烷基、二叔丁基甲基甲硅烷基、三苄基甲硅烷基、三对二甲苯基甲硅烷基、三苯基甲硅烷基和二苯基甲基甲硅烷基。优选的保护基团包括三烷基甲硅烷基，其中最优选三甲基甲硅烷基。

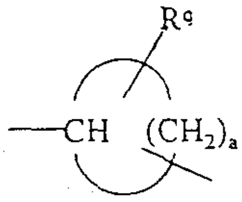
本发明的基础聚合物可非必要地包含选自如下通式 III 的重复单元:



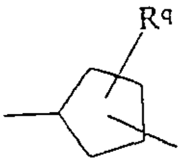
III

其中 R^9 至 R^{12} 独立地表示氢、线性或支化(C_1 至 C_{10})烷基，或选自如下基团的取代基：$-(A)_n-C(O)OR''$，$-(A)_n-OR''$，$-(A)_n-OC(O)R''$，$-(A)_n-OC(O)OR''$，$-(A)_n-C(O)R''$，$-(A)_n-OC(O)C(O)OR''$，$-(A)_n-O-A'-C(O)OR''$，$-(A)_n-OC(O)-A'-C(O)OR''$，$-(A)_n-C(O)O-A'-C(O)OR''$，$-(A)_n-C(O)-A'-OR''$，$-(A)_n-C(O)O-A'-OC(O)OR''$，$-(A)_n-C(O)O-A'-O-A'-C(O)OR''$，$-(A)_n-C(O)O-A'-OC(O)C(O)OR''$，$-(A)_n-C(R'')_2CH(R'')(C(O)OR'')$ 和 $-(A)_n-C(R'')_2CH(C(O)OR'')_2$；和 q 为 0 至 5，优选 0 或 1 的整数。部分 A 和 A'独立地表示选自二价烃基、二价环状烃基、二价含氧基团以及二价环醚和环二醚的二价桥连或间隔基团；n 为 0 或 1 的整数。当 n 为 0 时，显然 A 表示单共价键。术语二价是指在基团各末端处的自由价与两个不同基团连接。该二价烃基可由通式$-(C_dH_{2d})-$表示，其中 d 表示亚烷基链中的碳原子数并为 1 至 10 的整数。该二价烃基优选选自线性和支化(C_1 至 C_{10})亚烷基如亚甲基、亚乙基、亚丙基、亚丁基、亚戊基、亚己基、亚庚基、亚辛基、亚壬基和亚癸基。当为支化亚烷基时，应理解线性亚烷基链中的氢原子被线性或支化(C_1 至 C_5)烷基取代。

二价环烃基包括如下通式表示的取代和未取代(C_3 至 C_8) 环脂族部分:



其中 a 为 2 至 7 的整数和 R^q(当存在时)表示线性和支化(C_1 至 C_{10})烷基。优选的二价环亚烷基包括如下结构表示的环亚戊基和环亚己基部分:



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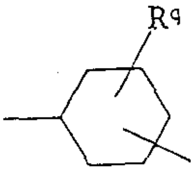
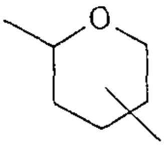


其中 R^q 为上面定义的。

优选的二价环状醚和二醚由如下结构表示:



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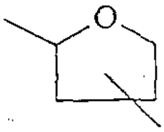

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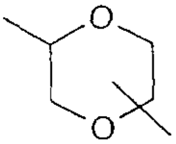
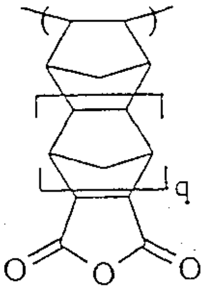


该二价含氧基团包括(C_2 至 C_{10})亚烷基醚和聚醚。(C_2 至 C_{10})亚烷基醚是指二价醚部分中的碳原子总数必须至少为 2 并不可超过 10。二价亚烷基醚由通式-亚烷基-O-亚烷基-表示，其中与氧原子键合的各亚烷基可以相同或不同，并选自亚甲基、亚乙基、亚丙基、亚丁基、亚戊基、亚己基、亚庚基、亚辛基和亚壬基。这一系列中最简单的二价亚烷基醚为基团$-CH_2-O-CH_2-$。优选的聚醚部分包括如下通式的二价基团:

$$-(CH_2(CH_2)_xO)_y-$$

其中 x 为 1 至 5 的整数，y 为 2 至 50 的整数，条件是聚醚间隔部分上的末端氧原子不与相邻基团上的末端氧原子直接连接形成过氧化物键。换言之，当聚醚间隔基与上面 R^9 至 R^{12} 中所列的任一含末端氧取代基连接时，不考虑过氧化物键(即$-O-O-$)。R^9 和 R^{12} 可与连接它们的环碳原子一起表示环状酸酐结构，如下面表示的:



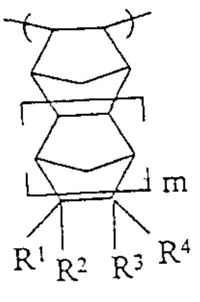
其中 q 为上面定义的。R″独立地表示线性和支化(C_1 至 C_{10}) 烷基、线性和支化(C_1 至 C_{10})烷氧基亚烷基、聚醚、单环和多环(C_4 至 C_{20})环脂族部分、环醚、环酮和环酯(内酯)。术语(C_1 至 C_{10})烷氧基亚烷基是指末端烷基通过醚氧原子与亚烷基部分连接。该基团是可一般性表示为-亚烷基-O-烷基的基于烃的醚部分，其中亚烷基和烷基独立地含 1 至 10 个碳原子，且各自为线性或支化的。该聚醚基团可由如下通式表示:

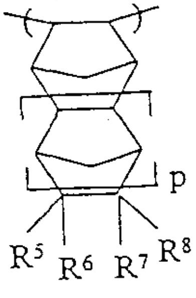
$$-(CH_2(CH_2)_xO)_y-R^a$$

其中 x 为 1 至 5 的整数，y 为 2 至 50 的整数，R^a 表示线性或支化(C_1 至 C_{10})烷基。优选的聚醚基团包括聚(环氧乙烷)和聚(环氧丙烷)。

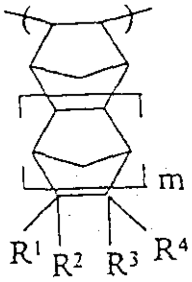
单环环脂族单环部分的例子包括环丙基、环丁基、环戊基、环己基等。环脂族多环部分的例子包括降冰片基、金刚烷基、四氢二聚环戊二烯基(三环[5.2.1.$0^{2,6}$]癸基)等。环醚的例子包括四氢呋喃基和四氢吡喃基部分。环酮的例子为 3-氧代环己酮基部分。

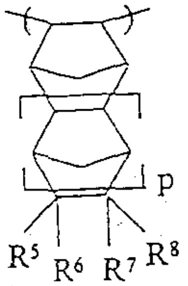
本发明的基础聚合物包括通式 I 和 II 给出的重复单元与非必要结合的通式 III 给出的重复单元。包括通式 I 和通式 III 的重复单元的基础聚合物也认为在本发明范围内。因此，本发明的基础聚合物包括如下重复单元:

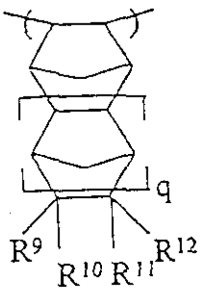




当包括通式 III 给出的非必要的重复单元时，本发明的基础聚合物包括如下重复单元:





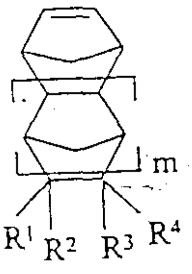


在上述聚合物中，R^1 至 R^{12}、m、p 和 q 为上面定义的，且 R^1 至 R^4 中至少一个必须为酸不稳定基团，R^5 至 R^8 中至少一个必须为含被保护羟基的部分。本发明的基础聚合物可包括这些重复单元的任何组合，只要在聚合物上存在含被保护羟基的侧基部分和酸不稳定侧基。

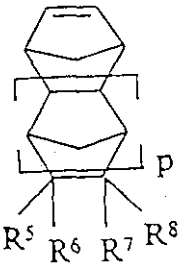
本发明的基础聚合物通常包括约 5 至约 95 mol％含酸不稳定侧基的多环重复单元，和约 95 至约 5 mol％含被保护羟基侧基部分的多环重复单元。本发明的聚合物可非必要地含约 5 至约 50 mol％通式 III 给出的重复单元。

本发明的基础聚合物优选为包括通过 2,3-键相互连接的多环重复单元的加成聚合物，其中该 2,3-键沿预聚的多环单体的降冰片烯型部分中所含的双键形成。

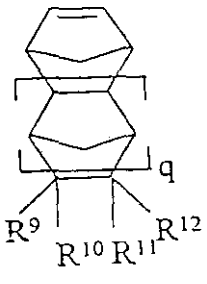
本发明的基础聚合物可在单或多组分 VIII 族过渡金属催化剂体系存在下由如下通式 Ia、IIa 和 IIIa 给出的适当官能化降冰片烯型单体聚合：



Ia，



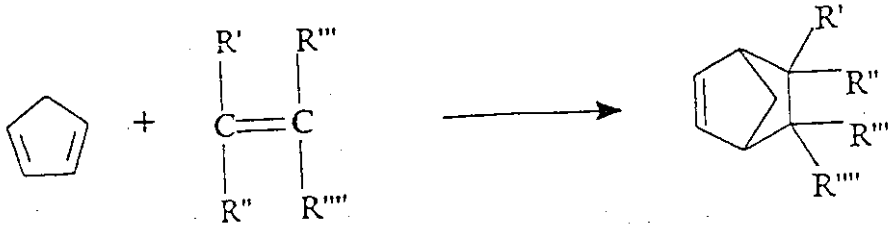
IIa，



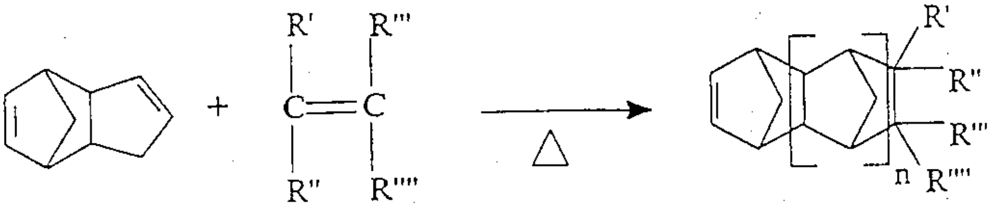
IIIa

其中 R^1 至 R^{12}、m、p 和 q 为上面描述的。

制备本发明取代多环单体的经济路径依赖于 Diels-Alder 反应，其中环戊二烯(CPD)或取代 CPD 与合适取代的亲二烯体在高温下反应形成取代多环加合物，该路径通常由如下反应方案表示：

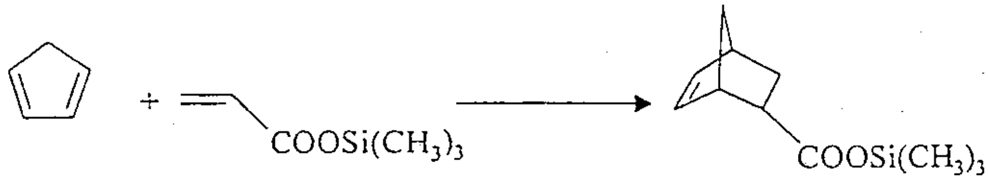


其它多环加合物可通过二聚环戊二烯(DCPD)在合适的亲二烯体存在下热裂解制备。该反应以 DCPD 裂解为 CPD 开始，接着进行 CPD 与亲二烯体的 Diels-Alder 加成，得到如下所示的加合物：



其中 R'至 R''''独立地表示上述通式 I、II 和 III 中对 R^1 至 R^{12} 定义的取代基。

例如，降冰片烯的三甲基甲硅烷基酯可通过环戊二烯与丙烯酰氧基三甲基硅烷按照如下反应方案进行 Diels-Alder 反应制备：



聚合这些单体的催化剂和方法描述于 1997 年 6 月 12 公开的国际专利申请 W097/33198（The BFGoodrich Company）中，该专利的全部内容这里作为参考引入。

用于制备本发明中使用的聚合物的单组分催化剂体系由如下通式表示：

$$E_nNi(C_6F_5)_2$$

其中 n 为 1 或 2，E 表示中性 2 电子给体配体。当 n 为 1 时，E 优选为π-芳烃配体如甲苯、苯和苯。当 n 为 2 时，E 优选选自二乙基醚、四氢呋喃(THF)和二噁烷。单体与催化剂在反应介质中的比例可为约 5000:1 至约 50:1。反应可在烃溶剂如环己烷、甲苯等中在温度约 0℃至约 70℃，优选 10℃至约 50℃，更优选约 20℃至约 40℃下进行。上

述通式的优选催化剂为(甲苯)双(全氟苯基)镍、(苯)双(全氟苯基)镍、(苯)双(全氟苯基)镍、双(四氢呋喃)双(全氟苯基)镍和双(二噁烷)双(全氟苯基)镍。

本发明的一个基本特征是，当这些单体加入聚合反应器中时通式IIa给出的单体的含羟基部分被保护。否则，含未保护羟基的部分趋于与VIII族金属催化剂反应，由此导致活性降低。

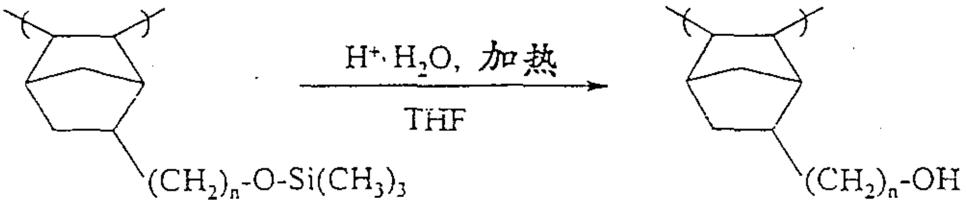
上述G中描述的保护基团通过本领域公知的工艺引入单体中并由例如T.W. Green和P.G.M. Wuts描述于*有机合成中的保护基团*（*Protective Groups In Organic Synthesis*），第二版，John Wiley & Sons, Inc., New York, 1991中。可使用其它保护基团，只要它们容易引入单体中，不与催化剂体系反应而抑制聚合反应，容易从被保护部分除去，且不进攻已除去保护的部分即可。该保护基团也应能够通过不进攻基础聚合物中的酸不稳定基团的脱保护试剂选择性除去。换言之，该保护基团具有的活化能比酸不稳定基团低。

该保护基团优选也应具有比酸不稳定部分低的活化能以确保保护基团断裂，同时保持酸不稳定基团原封不动。

在合成包括所需含被保护羟基的侧基部分的基础聚合物后，将该含被保护羟基的部分脱保护得到含醇、羧酸或苯酚的官能团。保护基团的除去也充分描述于本领域中，例如参见如上所述的*有机合成中的保护基团*中。代表性的脱保护反应列举如下:

醇:

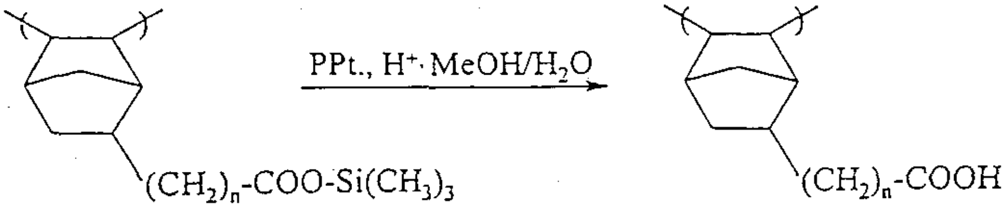
含被保护醇取代基（甲硅烷基醚）侧基的重复单元可通过在四氢呋喃溶剂存在下酸解脱保护，如下式所示:



其中 n 为 0 至 10 的整数。

羧酸:

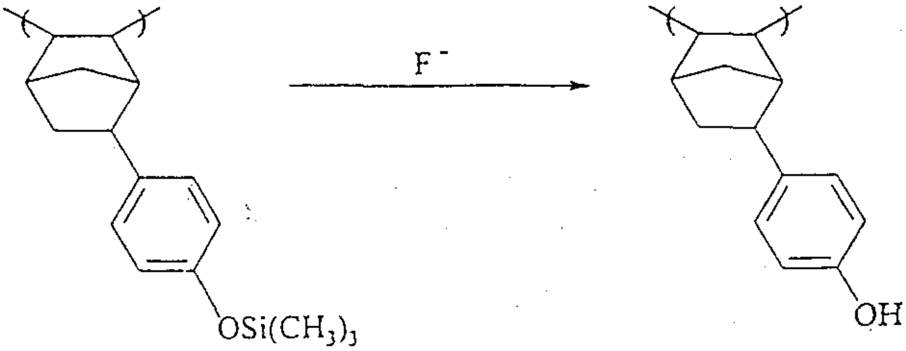
含被保护羧酸（甲硅烷基酯）取代基侧基的重复单元可按如上所述经酸解脱保护，或含该重复单元的基础聚合物可在甲醇水溶液中沉淀以对羧酸官能团进行水解。代表性脱保护反应列举如下:



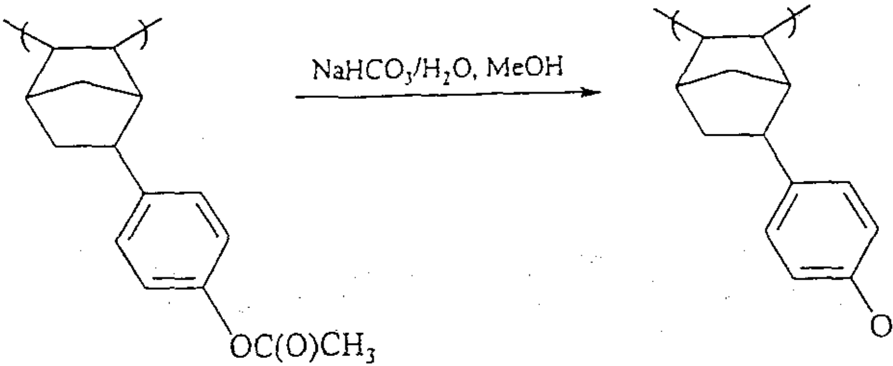
其中 n 为 0 至 10 的整数。如此生产的含酸的基础聚合物可在此时用于光刻胶应用或可按如下所述用共反应基团进行后官能化。

酚类:

含被保护苯酚基团（甲硅烷基醚）侧基的重复单元可通过将含相同基团的基础聚合物在酸性甲醇溶液中回流而脱保护。甲硅烷基醚保护基团中的三甲基甲硅烷基可由温和酸和碱或在氟离子（四烷基氟化铵）存在下开裂。反应方案可表示如下:



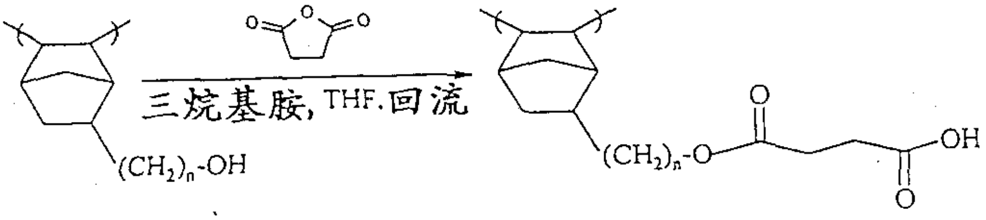
苯酚还可以乙酸苯基酯部分保护并在碳酸氢钠/甲醇水溶液存在下开裂生成苯酚，如下面所示的:



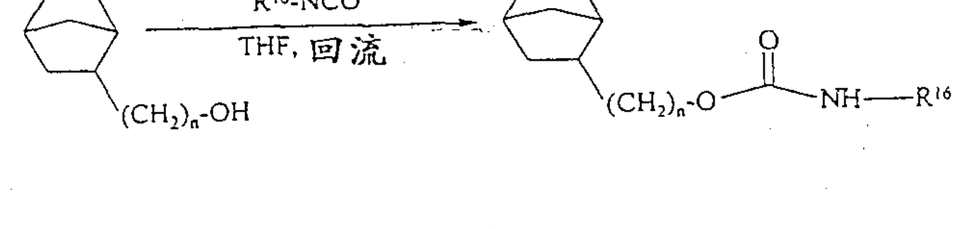
本发明的基础聚合物通过侧挂于基础聚合物中的多环重复单元上的脱保护醇和羧酸基团后官能化。本发明的脱保护基础聚合物可用增强光刻胶聚合物性能的任何共反应部分后官能化。

含醇侧基的基础聚合物可用琥珀酸酐，通式 R^{16}-NCO 的异氰酸酯、通式 $R^{16}-SO_2-O-SO_2-R^{16}$ 的磺酸酯和通式 $R^{16}-C(O)O(O)C-R^{16}$ 的共反应部分后官能化，其中在上述通式中，R^{16} 为线性或支化(C_1 至 C_{10})烷基、(C_6 至 C_{20})芳基、(C_7 至 C_{24})芳烷基，或通式-$(CH_2)_n-Si(R^{19})_3$ 表示的甲硅烷基，R^{19} 为线性或支化(C_1 至 C_{10})烷基、(C_6 至 C_{20})芳基、(C_7 至 C_{24})芳烷基，n 为 0 至 10 的整数。这里和整个说明书中使用的芳烷基是指具有线性或支化(C_1 至 C_{10})烷基取代基的芳基。芳基和芳烷基的代表性例子为苯基、甲苯基、二甲苯基等。代表性反应列举如下：

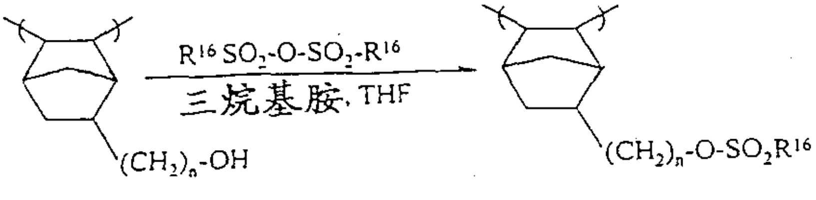
1.



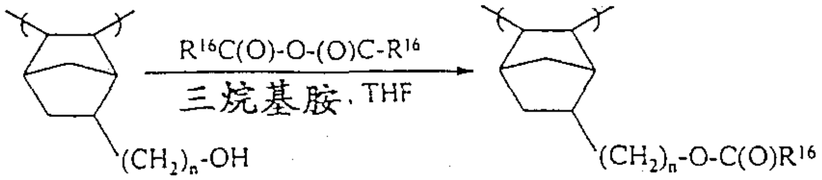
2.



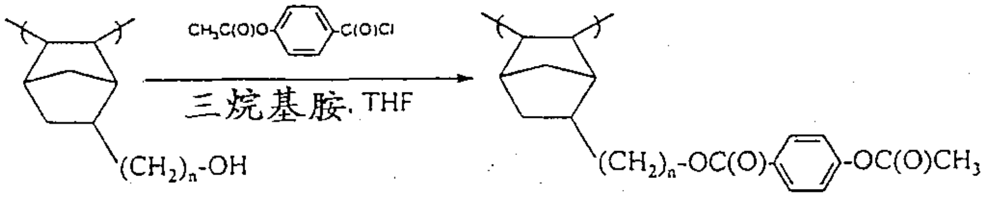
3.



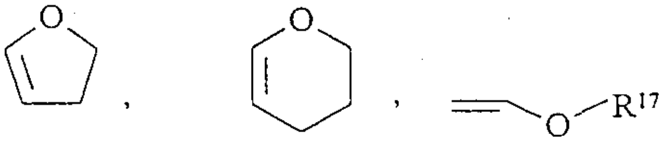
4.



5.

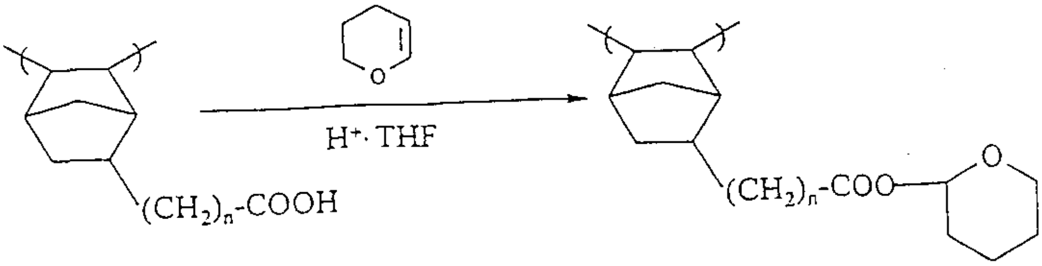


含羧酸侧基的基础聚合物可用线性和支化缩醛、环状缩醛、原碳酸酯和可与羧酸基团共反应的乙烯基醚官能化。合适的线性和支化缩醛取代基包括甲氧基甲氧基、乙氧基甲氧基、正丙氧基甲氧基、正丁氧基甲氧基、苯氧基甲氧基、异丙氧基甲氧基、叔丁氧基甲氧基和三氯乙氧基甲氧基。合适的环状缩醛取代基包括四氢呋喃氧基和四氢吡喃氧基。合适的原碳酸酯取代基包括三甲氧基甲氧基、三乙氧基甲氧基、三正丙氧基甲氧基和二乙氧基甲氧基。烯醇醚包括乙烯基醚、1-丙烯基醚、1-丁烯基醚、1, 3-丁二烯基醚和苯基乙烯基醚。代表性的共反应部分列举如下：

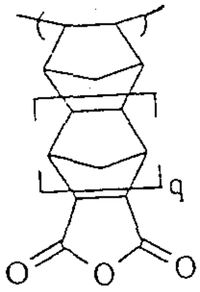


其中 R^{17} 表示线性或支化 (C_1 至 C_{10}) 烷基、(C_2 至 C_{10}) 链烯基或芳基。

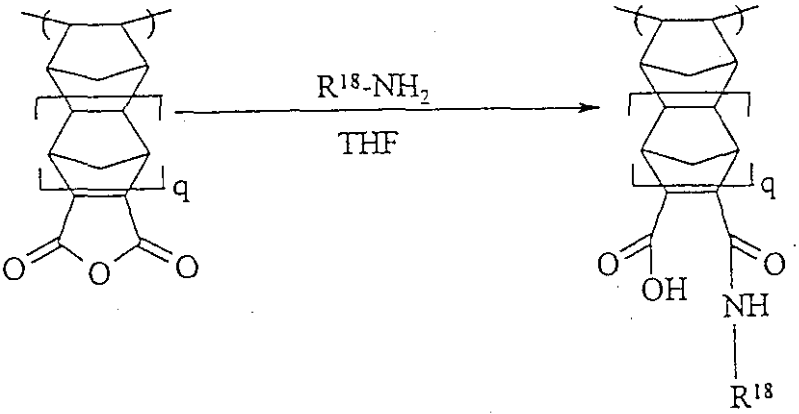
将上面的部分与所需的包括具有羧酸侧基的重复单元的基础聚合物反应。该反应在合适的溶剂中并在有助于进行该反应的温度下进行。羧酸部分的典型后官能化反应方案可表示如下：



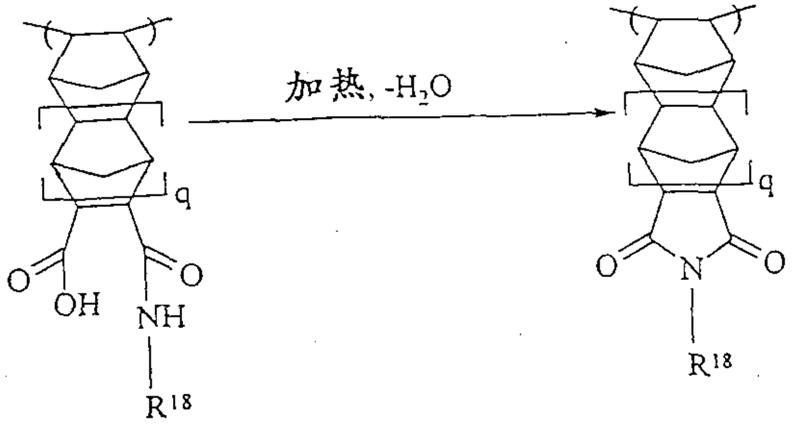
包括通式 I 和通式 III 的重复单元的基础聚合物可进行后官能化，只要通式 III 的多环重复单元上的取代基适合该后反应，且后反应条件对通式 I 的共重复单元上的酸不稳定基团无不利影响即可。已发现下面通式 III 的官能团（其中 R^9 和 R^{12} 与连接它们的碳原子一起形成环状酸酐）是进行后官能化反应的优良平台。



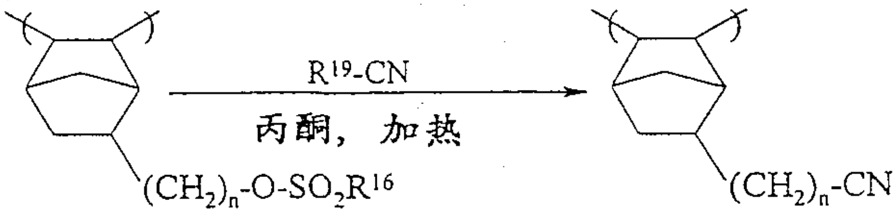
环状酸酐官能团可与胺 R^{18}-NH_2 或醇反应得到二官能酸/酰胺或二官能酸/酯。酸酐官能团向二官能酸/酰胺的转化示意如下：



其中 R^{18} 为线性或支化 (C_1 至 C_{10}) 烷基、(C_6 至 C_{20}) 芳基或芳烷基。如此获得的二官能重复单元可通过在合适的溶剂中进行缩合反应环化，生成酰亚胺官能团，如下式所示：

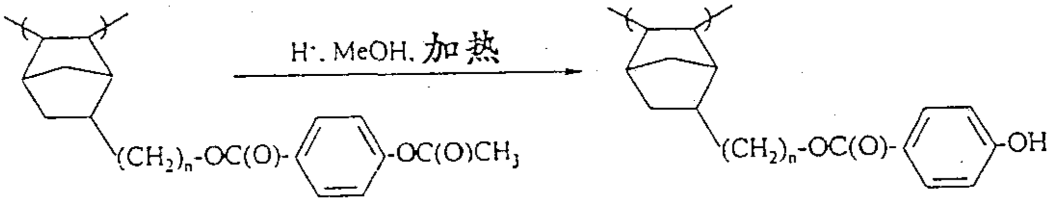


除了后官能化含所需的醇和羧酸的基础聚合物组合物外，还认识到本发明的后官能化聚合物组合物可进一步官能化以将侧基取代基引入聚合物主链中。例如，可通过磺酰基酯取代的聚合物与氰化物盐，例如氰化钠或有机腈如三甲基甲硅烷基腈在卤化物盐存在下反应生成具有腈取代的重复单元的聚合物而将腈基团引入聚合物中。该反应可表示如下：



其中 R^{19} 为能够通过卤化物盐如氯化钠、氟化钠等开裂的有机基团。

在另一反应中，上面等式 5 的后官能化产物可在酸性甲醇溶液存在下进一步反应使乙酸酯取代基自苯基环开裂，由此获得相应的苯酚。该反应可表示如下：



上述后官能化反应可通过使包括具有反应性侧基部分的重复单元的基础聚合物与所需的共反应部分在合适的溶剂中在诱导该反应且对反应物或所需产物无过度影响的温度下反应而进行。合适的溶剂包括芳烃溶剂如苯、氯苯、二甲苯和甲苯；卤代烃溶剂如二氯乙烷、二氯甲烷和四氯化碳；酸醚如乙酸乙酯和乙酸丁酯；和醚如四氢呋喃(THF)。溶剂的选取取决于反应剂和所需的反应条件。优选的溶剂为醚，如二噁烷和 THF。将要反应的基础聚合物或官能化聚合物与合适的共反应剂一起溶于合适的溶剂中。然后将这些反应剂在搅拌下在合适的温度范围内反应，以进行有效的官能化反应。反应温度可为约-100℃至回流温度，取决于该反应的特点和溶剂。完成官能化后，将聚合物从反应介质中分离并按照常规工艺纯化。本发明含羟基部分的后官能化程

度通常为10至100 mol%，优选20至80 mol%，更优选30至70 mol%。

本发明的光刻胶组合物包括公开的多环组合物、溶剂和光敏性酸生成剂（光引发剂）。可非必要地加入为组合物重量的至多约20 wt%的溶解抑制剂。合适的溶解抑制剂是胆酸叔丁酯（t-butyl chelate）（J.V. Crivello等人，化学放大电子束光刻胶，*化学材料*，1996,8,376-381）。

经辐射曝光后，辐射敏感性酸生成剂产生强酸。合适的光致酸生成剂包括三氟甲磺酸盐(triflate)（例如三氟甲磺酸三苯基锍盐）、焦棓酚（例如焦棓酚的三甲磺酸酯）；鎓盐如三芳基锍和二芳基碘鎓的六氟锑酸盐、六氟砷酸盐、三氟甲磺酸盐；羟基酰亚胺的酯、α,α'-双磺酰基-重氮甲烷、硝基取代的苄醇的磺酸酯和萘醌-4-重氮化物(diazide)。其它合适的光致酸生成剂公开于Reichmanis等人，*化学材料*，3，395，(1991)中。含三芳基锍或二芳基碘鎓盐的组合物是优选的，因为它们对深UV光(193-300 nm)敏感并得到非常高分辨率的影像。最优选的是未取代和对称或非对称取代的二芳基碘鎓或三芳基锍盐。光致酸引发剂组分占约1至100 w/w%（按聚合物计）。优选的浓度范围为5至50 w/w%。

本发明的光刻胶组合物非必要地含有能够使光致酸引发剂对从中UV至可见光的更长波长的光敏感的增感剂。根据预定用途，这些增感剂包括多环芳烃如芘和苝。光致酸引发剂的增感作用是公知的并描述于US 4,250,053、4,371,605和4,491,628中，这些专利这里都作为参考引入。本发明对增感剂或光致酸引发剂的具体类型无限制。

本发明还涉及在基材上形成正色调光刻胶影像的方法，包括如下步骤：(a)用包括本发明正色调光刻胶组合物的薄膜涂布基材；(b)对该薄膜进行成像辐射曝光；和(c)对影像进行显影。

第一个步骤涉及用包括溶于合适溶剂中的正色调光刻胶组合物的薄膜涂布基材。合适的基材包括硅、陶瓷、聚合物等。合适的溶剂包括丙二醇甲基醚乙酸酯（PGMEA）、环己酮、丁酸乳酸酯、乳酸乙酯等。

该薄膜可用本领域已知工艺如旋涂或喷涂，或刮涂涂于基材上。在薄膜辐射曝光之前，优选将薄膜加热至约90至150℃的高温并保持约1分钟的短时间。在该方法的第二个步骤中，将薄膜进行辐射成像曝光，所述辐射合适地为电子束或电磁辐射，优选电磁辐射，如紫外线或x-射线，优选合适地波长为约193至514 nm，优选约193至248 nm的紫外线辐射。合适的辐射源包括汞、汞/氙和氙灯，氟化氩和氟化氪激光，x-射线或e-束。通过辐射敏感性酸生成剂吸收辐射，由此在曝光区域生成游离酸。游离酸催化共聚物的酸不稳定侧基的开裂，使共聚物从溶解抑制剂转化为溶解增强剂，由此增加曝光后的光刻胶组合物在碱水溶液中的溶解性。在薄膜辐射曝光之后，优选将薄膜再加热至约90至150℃的高温并保持约1分钟的短时间。

第三个步骤涉及用合适的溶剂对正色调影像显影。合适的溶剂包括碱水溶液，优选无金属离子的碱水溶液，如四甲基氢氧化铵或胆碱。本发明的组合物提供具有高对比度和直壁的正影像。本发明组合物的溶解性能还特别可通过简单改变共聚物的组成进行变化。

本发明还涉及一种集成电路组件，如通过本发明方法制备的集成电路芯片、多芯片组件或电路板。本发明的集成电路组件包括通过如下步骤在基材上形成的电路：(a)用包括本发明正色调光刻胶组合物的薄膜涂布基材；(b)对该薄膜进行成像辐射曝光；(c)对影像进行显影，使基材暴露；和(d)通过本领域公知的技术在基材上的显影薄膜内形成电路。

基材曝光后，可通过本领域已知技术如蒸发、溅射、电镀、化学蒸气淀积或激光诱发淀积用导电物质如导电金属涂布基材，在曝光区域形成电路图形。可对薄膜表面打磨以除去过量的导电物质。介电物质也可按类似方式在制备电路期间淀积。可将无机离子如硼、磷或砷在制备p或n掺杂电路晶体管的方法中引入基材中。形成电路的其它方式是本领域熟练技术人员公知的。

下面的实施例将详细描述本发明某些组合物的制备方法和用途。详细描述的制备方法落入上述更一般性描述的制备方法范围内并起到

举例说明的作用。给出的这些实施例仅用于说明目的，并非用于限制本发明范围。

实施例1

合成降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇共聚物(50/50摩尔比)

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入17.6 g (0.089 mol)三甲基甲硅烷基保护的降冰片醇、17.4 g (0.089 mol)降冰片烯的叔丁基酯和80 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.43 g (0.895 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入15 ml甲苯中制备催化剂溶液。搅拌下聚合5小时后，加入溶于10 ml丙酮中的0.255 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入丙酮中使聚合物沉淀。将沉淀出的聚合物过滤、再溶于四氢呋喃中，并用Amberlyst®IR-131（Rohm& Haas)-聚苯乙烯/磺酸基湿离子交换树脂处理。将所得聚合物溶液浓缩并沉淀入甲醇中。将该聚合物过滤并真空干燥过夜。聚合物的产量为15.3 g (44%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 47,000, Mw=84,000。IR清楚显示不存在任何羟基。^{1}H NMR显示该聚合物组成与初始单体加料比非常接近。

实施例2

由降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇共聚物(50/50摩尔比)

合成降冰片烯的叔丁基酯/降冰片醇共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入17.6 g (0.089 mol)三甲基甲硅烷基保护的降冰片醇、17.4 g (0.089 mol)降冰片烯的叔丁基酯和80 ml甲苯。在室温下向该反应溶液中通过注射器加入镍

催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.43 g (0.895 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入15 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于10 ml丙酮中的0.255 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含少量去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为21.4 g (61%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 36,000, Mw=68,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例3

由碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(70/20/10)合成碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入11.5 g (0.061 mol) 碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯、3.38 g (0.017 mol) 降冰片烯的叔丁基酯、1.71 g (8.7 mol)三甲基甲硅烷基保护的降冰片醇和40 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.211 g (0.435 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.123 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再

溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为16.2 g (95%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 45,000, Mw=85,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例4

由碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(60/30/10摩尔比)合成碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入10.25 g (0.052 mol) 碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯、5.07 g (0.026 mol) 降冰片烯的叔丁基酯、1.71 g (8.7 mol)三甲基甲硅烷基保护的降冰片醇和40 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.211 g (0.435 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.123 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为15.3 g (90%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 40,600, Mw=83,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例5

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(50/40/10摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入25.1 g(0.128 mol)碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、19.88 g (0.102 mol)降冰片烯的叔丁基酯、5.02 g (0.026 mol)三甲基甲硅烷基保护的降冰片醇和40 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.620 g (1.28 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.3636 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为35.9 g (72%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 34,600, Mw=68,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例6

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(50/35/15摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入12.5 g(0.638

mol）碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、8.68 g（0.045 mol）降冰片烯的叔丁基酯、3.76 g（0.019 mol）三甲基甲硅烷基保护的降冰片醇和40 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.301 g（0.638 mmol）$(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.181 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为20.00 g（80％）。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn ＝ 34,300，Mw=72,000。IR清楚显示存在羟基。^1H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例7

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(50/30/20摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入6.5 g（0.338 mol）碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、3.86 g（0.019 mol）降冰片烯的叔丁基酯、2.6 g（0.013 mol）三甲基甲硅烷基保护的降冰片醇和40 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.301 g（0.638 mmol）$(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.181 g 1,2-环己二酮二肟的

溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为21.23 g (85 %)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 34,300, Mw=72,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例8

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(50/25/25摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入12.5 g(0.638 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、6.21 g (0.032 mol)降冰片烯的叔丁基酯、6.28 g (0.032 mol)三甲基甲硅烷基保护的降冰片醇和62 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.309 g (0.64 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.182 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为16.6 g (66 %)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子

量为Mn = 41,300, Mw=75,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例9

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(50/25/25摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入12.5 g(0.638 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、6.21 g (0.032 mol)降冰片烯的叔丁基酯、6.28 g (0.032 mol)三甲基甲硅烷基保护的降冰片醇和62 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.309 g (0.64 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.182 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为16.6 g (66%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 41,300, Mw=75,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例10

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(30/50/20摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇

三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入4.85 g（0.024 mol）碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、8.0 g（0.041 mol）降冰片烯的叔丁基酯、3.23 g（0.016 mol）三甲基甲硅烷基保护的降冰片醇和30 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.199 g（0.412 mmol）$(CH_3C_6H_5)Ni(C_6F_5)_2$加入15 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.117 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合后。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为9.7 g（60％）。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 31,300，Mw=65,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例11

由乙酸双环[2.2.1]庚-5-烯－2－甲酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物（40/40/20摩尔比）合成乙酸双环[2.2.1]庚-5-烯－2－甲酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入1.10 g（6.65 mmol）乙酸双环[2.2.1]庚-5-烯－2－甲酯、1.30 g（6.7 mmol）降冰片烯的叔丁基酯和0.60 g（3.08 mmol）三甲基甲硅烷基保护的降冰片醇。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.04g（0.083 mmol）$(CH_3C_6H_5)Ni(C_6F_5)_2$加入7 ml甲苯中制备催化剂溶液。在搅拌下聚合5小

时后，加入溶于5 ml丙酮中的0.024 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为0.72 g (24%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 19,000，Mw=77,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例12

由草酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(70/20/10摩尔比)合成草酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入16.02 g(0.071 mol)草酸双环[2.2.1]庚-5-烯-2-甲基乙基酯、3.97 g (0.02 mol)降冰片烯的叔丁基酯、2.00 g (0.01 mol)三甲基甲硅烷基保护的降冰片醇和55 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.247 g (0.51 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.145 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为20.3 g (92

%）。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 19,000，Mw=77,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例13

由降冰片烯的乙基酯/三甲基甲硅烷基保护的降冰片醇三元共聚物(70/20/10摩尔比)合成降冰片烯的乙基酯/降冰片醇共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入16.05 g(0.02 mol) 降冰片烯的乙基酯、18.96 g (0.097 mol)三甲基甲硅烷基保护的降冰片醇和90 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.47 g (0.97 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.275 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到螯合的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩并倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将一部分沉淀的聚合物再溶于含5 ml去离子水的四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为28.5 g (81%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 49,000，Mw=80,000。IR清楚显示存在羟基。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例14

用琥珀酸酐将降冰片烯的叔丁基酯/降冰片醇共聚物(50/50摩尔比)转化为降冰片烯的叔丁基酯/琥珀酸单(降冰片基甲基)酯共聚物

向装有回流冷凝器和温度计的干燥3-颈 50 ml圆底烧瓶中放入0.5 g实施例2中制备的降冰片烯的叔丁基酯/降冰片醇共聚物，接着加入

0.014 g (0.14 mmol)琥珀酸酐、10 ml四氢呋喃和4.2 μl (0.028 mmol)1，8－二氮杂双环[5.4.0]十一碳-7-烯。将该混合物回流3小时，然后用二甲基甲酰胺(DMF)稀释，并在稀乙酸溶液中沉淀。将该沉淀的聚合物用甲醇洗涤除去未反应的琥珀酸酐，过滤并在真空下干燥过夜。将该聚合物用IR和NMR表征。观察到聚合物的分子量为Mn=49,000，Mw=80,000。IR和^{1}H清楚地显示存在酸官能团。

实施例15

用琥珀酸酐将碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物(50/30/20摩尔比)转化为碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/琥珀酸单(降冰片基甲基)酯共聚物

向装有回流冷凝器和温度计的干燥3-颈 50 ml圆底烧瓶中放入0.5 g实施例7中获得的碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物，接着加入0.042 g (0.14 mmol)琥珀酸酐、10 ml四氢呋喃和57 l (0.379 mmol)1，8－二氮杂双环[5.4.0]十一碳-7-烯。将该混合物回流3小时，然后冷却。将该聚合物在稀乙酸溶液中沉淀。将该沉淀的聚合物用甲醇洗涤除去未反应的琥珀酸酐，过滤并在真空下干燥过夜。将该聚合物用IR和NMR表征。IR清楚地显示羟基官能团转化为酸官能团。

实施例16

用琥珀酸酐将碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物(50/40/10摩尔比)转化为碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/琥珀酸单(降冰片基甲基)酯共聚物

向装有回流冷凝器和温度计的干燥3-颈 50 ml圆底烧瓶中放入0.5 g实施例5中获得的碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物，接着加入0.73 g (7.3 mmol)琥

珀酸酐、35 ml四氢呋喃和325 l (2.18 mmol)1，8－二氮杂双环[5.4.0]十一碳-7-烯。将该混合物回流3小时，然后冷却。将该聚合物在稀乙酸溶液中沉淀。将该沉淀的聚合物用甲醇洗涤除去未反应的琥珀酸酐，过滤并在真空下干燥过夜。将该聚合物用IR和NMR表征。IR清楚地显示羟基官能团转化为酸官能团。

实施例17

用琥珀酸酐将碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物(50/35/15摩尔比)转化为碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/琥珀酸单(降冰片基甲基)酯共聚物

向装有回流冷凝器和温度计的干燥3-颈 250 ml圆底烧瓶中放入16.6 g实施例6中获得的碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物，接着加入1.58 g (0.016 mmol)琥珀酸酐、100 ml四氢呋喃和710 l (4.75 mmol)1，8－二氮杂双环[5.4.0]十一碳-7-烯。将该混合物回流3小时，然后冷却，用四氢呋喃稀释，并将该聚合物在稀乙酸溶液中沉淀。将该沉淀的聚合物用甲醇洗涤除去未反应的琥珀酸酐，过滤并在真空下干燥过夜。将该干燥的聚合物溶于四氢呋喃中，并用Amberlyst®干燥离子交换树脂处理，过滤、浓缩并在甲醇中沉淀。将该聚合物用IR、NMR和GPC表征。IR清楚地显示羟基官能团转化为酸官能团。测得聚合物的分子量为Mn=32，000和Mw=84，000。

实施例18

用琥珀酸酐将碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物(50/25/25摩尔比)转化为碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/琥珀酸单(降冰片基甲基)酯共聚物

向装有回流冷凝器和温度计的干燥3-颈 250 ml圆底烧瓶中放入

14.5 g实施例8中获得的碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物，接着加入0.83 g (8.27 mmol)琥珀酸酐、100 ml四氢呋喃和370 l (2.48 mmol) 1,8－二氮杂双环[5.4.0]十一碳-7-烯。将该混合物回流3小时，然后冷却，用四氢呋喃稀释，并将该聚合物在稀乙酸溶液中沉淀。将该沉淀的聚合物用甲醇洗涤除去未反应的琥珀酸酐，过滤并在真空下干燥过夜。将该干燥的聚合物溶于四氢呋喃中，并用Amberlyst®干燥离子交换树脂处理，过滤、浓缩并在甲醇中沉淀。将该聚合物用IR、NMR和GPC表征。IR清楚地显示羟基官能团转化为酸官能团。测得聚合物的分子量为Mn=43,000和Mw=86,000。

实施例19

用琥珀酸酐将草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物(50/25/25摩尔比)转化为草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/琥珀酸单(降冰片基甲基)酯共聚物

向装有回流冷凝器和温度计的干燥3-颈 250 ml圆底烧瓶中放入16.0 g实施例12中获得的草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片醇三元共聚物，接着加入2.0 g (0.02 mmol)琥珀酸酐、100 ml四氢呋喃和897 l (6.0 mmol) 1,8－二氮杂双环[5.4.0]十一碳-7-烯。将该混合物回流3小时，然后冷却，并将该聚合物在稀乙酸溶液中沉淀。将该沉淀的聚合物用甲醇洗涤除去未反应的琥珀酸酐，过滤并在真空下干燥过夜。将该干燥的聚合物溶于四氢呋喃中，并用Amberlyst®干燥离子交换树脂处理，过滤、浓缩并在甲醇中沉淀。将该聚合物用IR、NMR和GPC表征。IR清楚地显示羟基官能团转化为酸官能团。测得聚合物的分子量为Mn=68,000和Mw=149,000。

实施例20

由草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降

冰片烯的三甲基甲硅烷基酯三元共聚物(50/40/10摩尔比)合成草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入14.00 g (0.063 mol) 草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、9.70 g (0.05 mol) 降冰片烯的叔丁基酯、2.63 g (0.013 mol)降冰片烯的三甲基甲硅烷基酯和65 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.303 g (0.62 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后, 加入溶于5 ml丙酮中的0.178 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到沉淀的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物, 将滤液浓缩然后倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团, 将沉淀的聚合物再溶于四氢呋喃中, 并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液过滤、浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为13.4 g (51%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 33,000, Mw=85,000。IR清楚显示存在酸官能团。^1H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例21

由草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的三甲基甲硅烷基酯共聚物(50/50摩尔比)合成草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片基羧酸共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入1.03 g (4.6 mmol) 草酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、0.962 g (4.57 mmol)降冰片烯的三甲基甲硅烷基酯, 接着加入5 ml环己烷和1 ml乙酸乙酯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 200/1)。在干燥箱内通过将0.022 g (0.046 mmol)

$(CH_3C_6H_5)Ni(C_6F_5)_2$加入5.0 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时并将溶液倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将沉淀的聚合物再溶于四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。聚合物的总产量为0.64 g (32%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 49,000, Mw=142,000。IR清楚显示存在酸官能团且该聚合物组成与初始单体加料比非常接近。

实施例22

由碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯三元共聚物(50/40/10摩尔比)合成碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入21.00 g (0.11 mol) 碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯、16.6 g (0.085 mol) 降冰片烯的叔丁基酯、4.5 g (0.021 mol)降冰片烯的三甲基甲硅烷基酯和430 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 100/1)。在干燥箱内通过将1.038 g (2.14 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.61 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到沉淀的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩然后倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将沉淀的聚合物再溶于四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液浓缩并在1N乙酸/甲醇溶液中沉淀。将所得聚合物过滤并真空干燥过夜。聚合物的总产量为31 g (75%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =18,000, Mw=36,000。IR清楚显示存在酸官能团。 ^1H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例23

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯三元共聚物(40/40/20摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入17.94 g (0.191 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、17.76 g (0.091 mol) 降冰片烯的叔丁基酯、9.6 g (0.046 mol)降冰片烯的三甲基甲硅烷基酯和288 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 100/1)。在干燥箱内通过将1.108 g (2.28 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于5 ml丙酮中的0.65 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到沉淀的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩然后倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将沉淀的聚合物再溶于四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液过滤、浓缩并在己烷并中沉淀。将沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为29 g (64%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =17,000, Mw=33,700。IR清楚显示存在酸官能团。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例24

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯三元共聚物(50/25/25摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入19.74 g (0.1 mol)

碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、9.75 g (0.501 mol)降冰片烯的叔丁基酯、10.56 g (0.050 mol)降冰片烯的三甲基甲硅烷基酯和253 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：100/1）。在干燥箱内通过将0.973 g (2.01 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，将聚合物溶液用Amberlite® IRC-718 (Rohm & Haas)基于亚氨基乙酸的螯合树脂处理，接着用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时后。将所得聚合物溶液过滤、浓缩并在己烷中沉淀。将沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为27.6 g (68%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =19,000, Mw=41,700。IR清楚显示存在酸官能团。^1H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例25

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯的三元共聚物(50/35/15摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸三元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入21.34 g (0.11 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、14.8 g (0.076 mol)降冰片烯的叔丁基酯、6.86 g (0.033 mol)降冰片烯的三甲基甲硅烷基酯和273 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例：100/1)。在干燥箱内通过将1.055 g (2.17 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，将聚合物溶液用Amberlite® IRC-718螯合树脂处理，接着用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时后。将所得聚合物溶液过滤、浓缩并在己烷中沉淀。将沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为31.6 g (74%)。将该聚合物进一步用

GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =19,000，Mw=40,000。IR清楚显示存在酸官能团。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例26

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯/四环十二碳烯的乙基酯四元共聚物(25/35/15/25摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸/四环十二碳烯的乙基酯四元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入10.68 g (0.052 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、12.64 g (0.054 mol)四环十二碳烯的乙基酯、14.08 g (0.076 mol)降冰片烯的叔丁基酯、6.86 g (0.033 mol)降冰片烯的三甲基甲硅烷基酯和110 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：100/1）。在干燥箱内通过将1.055 g (2.17 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，将聚合物溶液用Amberlite® IRC-718 螯合树脂处理，接着用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时后。将所得聚合物溶液过滤、浓缩并在己烷中沉淀。将沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为27.9 g (62％)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =12,000，Mw=26,000。IR清楚显示存在酸官能团。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例27

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯/四环十二碳烯的乙基酯四元共聚物(25/25/25/25摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/

降冰片烯的叔丁基酯/降冰片基羧酸/四环十二碳烯的乙基酯四元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入11.78 g (0.06 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、13.94 g (0.06 mol) 四环十二碳烯的乙基酯、11.66 g (0.06 mol)降冰片烯的叔丁基酯、12.6 g (0.06 mol)降冰片烯的三甲基甲硅烷基酯和110 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：100/1）。在干燥箱内通过将1.16 g (2.17 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，将聚合物溶液用Amberlite® IRC-718螯合树脂处理，接着用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时后。将所得聚合物溶液过滤、浓缩并在己烷中沉淀。将沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为26.1 g (52%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =12,000, Mw=26,000。IR清楚显示存在酸官能团。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例28

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯/草酸双环[2.2.1]庚-5-烯－甲基乙基酯四元共聚物(30/30/30/10摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸/草酸双环[2.2.1]庚-5-烯－甲基乙基酯四元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入10.31 g (0.053 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、11.78 g (0.052 mol) 草酸双环[2.2.1]庚-5-烯－甲基乙基酯、10.21 g (0.052 mol)降冰片烯的叔丁基酯、3.68 g (0.017 mol)降冰片烯的三甲基甲硅烷基酯和110 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：100/1）。在干燥箱内通过将0.849 g (1.75 mmol)

$(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，将聚合物溶液用Amberlite® IRC-718 螯合树脂处理，接着用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时后。将所得聚合物溶液过滤、浓缩并在己烷中沉淀。将沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为29.1 g (81%)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn =25,000, Mw=68,000。IR清楚显示存在酸官能团。^1H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例29

由碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯/双环[2.2.1]庚-5-烯-2-甲基甲基醚四元共聚物(30/30/30/10摩尔比)合成碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸/双环[2.2.1]庚-5-烯-2-甲基甲基醚四元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入13.11 g (0.067 mol) 碳酸双环[2.2.1]庚-5-烯-2-甲基乙基酯、9.23 g (0.067 mol)双环[2.2.1]庚-5-烯-2-甲基甲基醚、12.98 g (0.067 mol)降冰片烯的叔丁基酯、4.68 g (0.022 mol)降冰片烯的三甲基甲硅烷基酯和110 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液(单体与催化剂的比例: 100/1)。在干燥箱内通过将1.08 g (2.23 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于10 ml丙酮中的0.63 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到沉淀的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩然后倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将沉淀的聚合物再溶于四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液过滤、浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为31.7 g (79%)。将该聚合物进一

步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 18,000，Mw=35,700。IR清楚显示存在酸官能团。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例30

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片烯的三甲基甲硅烷基酯/双环[2.2.1]庚-5-烯四元共聚物(50/30/10/10摩尔比)合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降冰片基羧酸/双环[2.2.1]庚-5-烯四元共聚物

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入20.99 g (0.107 mol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、2.01 g (0.021 mol) 双环[2.2.1]庚-5-烯、12.47 g (0.064 mol)降冰片烯的叔丁基酯、4.5 g (0.021 mol)降冰片烯的三甲基甲硅烷基酯和110 ml甲苯。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：100/1）。在干燥箱内通过将1.03 g (2.14 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入10 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于10 ml丙酮中的0.61 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到沉淀的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩然后倒入甲醇中使聚合物沉淀。为除去三甲基甲硅烷基保护基团，将沉淀的聚合物再溶于四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液过滤、浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为34.5 g (86％)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 20,000，Mw=46,700。IR清楚显示存在酸官能团。^{1}H NMR显示不存在三甲基甲硅烷基且该聚合物组成与初始单体加料比非常接近。

实施例31

由碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/降

冰片基羧酸三元共聚物(50/25/25摩尔比)

引入四氢吡喃基保护基团

在氮气气氛下向装有搅拌棒的50 ml烧瓶中加入5g实施例24获得的羧酸三元共聚物、3 g Amberlyst®IR-15干离子交换树脂和15 ml 四氢呋喃。在室温下向该反应溶液中用注射器加入8 ml 二氢吡喃。将该溶液慢慢加热回流5小时。将所得聚合物溶液冷却、过滤、浓缩并沉淀入己烷中。将该沉淀的聚合物过滤并真空干燥过夜。将获得的树脂进行IR分析。预期聚合物中的酸官能团进行酯化反应，生成四氢吡喃氧基羰基。

实施例32

合成碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯/降冰片烯的叔丁基酯/内降冰片烯二酸酐（endonadic anhydride）三元共聚物并将酸酐官能团后改性为脂族酰亚胺官能团 (50/40/10摩尔比)

在氮气气氛下向装有搅拌棒的玻璃管形瓶中加入1.56 g (7.95 mmol) 碳酸双环[2.2.1]庚-5-烯－2－甲基乙基酯、12.64 g (0.054 mmol) 四环十二碳烯的乙基酯、1.23 g (6.36 mmol)降冰片烯的叔丁基酯、在5 ml甲苯中的0.26 g (1.59 mmol)新制干燥的内降冰片烯二酸酐。在室温下向该反应溶液中通过注射器加入镍催化剂溶液（单体与催化剂的比例：200/1）。在干燥箱内通过将0.0383 g (0.08 mmol) $(CH_3C_6H_5)Ni(C_6F_5)_2$加入5 ml甲苯中制备催化剂溶液。在搅拌下聚合5小时后，加入溶于10 ml丙酮中的0.023 g 1,2-环己二酮二肟的溶液以使Ni催化剂螯合。观察到沉淀的Ni配合物立即沉淀。将该溶液搅拌过夜、过滤除去螯合的配合物，将滤液浓缩然后倒入甲醇中使聚合物沉淀。将沉淀的聚合物再溶于四氢呋喃中，并用Amberlyst®IR-15干离子交换树脂在50℃下处理5小时。将所得聚合物溶液过滤、浓缩并沉淀入甲醇中。将该沉淀的聚合物过滤并真空干燥过夜。聚合物的总产量为1.1 g (36％)。将该聚合物进一步用GPC、IR和NMR表征。观察到该聚合物的分子量为Mn = 23,000, Mw=49,000。IR清楚显示存在酸官能团。^{1}H NMR

显示聚合物组成与初始单体加料比非常接近。

实施例33

将实施例32中获得的聚合物通过与脂族胺如环己胺反应进一步后官能化为酰胺酸。在氮气气氛下向装有搅拌棒的50 ml烧瓶中加入1 g含酸酐的三元共聚物和15 ml四氢呋喃。在室温下用注射器向反应溶液中加入5 ml环己胺。将溶液在室温下搅拌5小时。将所得聚合物溶液冷却，用乙酸酐、吡啶混合物在60℃下进行酰亚胺化，并在甲醇中沉淀。将沉淀的聚合物过滤并真空干燥过夜。

实施例34

4-羟基苄基醇与聚（降冰片烯甲醇-co-降冰片烯叔丁酯）(50/50摩尔比)反应

向装有搅拌棒的100 ml圆底烧瓶中加入1.35 g 共聚物和20 ml THF。聚合物溶解后，加入4-羟基苄基醇(0.67 g, 5 mmol）。将反应剂在室温下搅拌10分钟以确保完全溶解。将HCl (4滴)加入该溶液中。反应液在室温下搅拌20小时。将该聚合物通过如下方法分离：在水中沉淀、过滤、在80℃的真空烘箱中干燥24小时。所得聚合物的收率是定量的。NMR和IR证实苄基与聚合物连接。

实施例35

1-金刚烷异氰酸酯与聚(降冰片烯甲醇-co-降冰片烯叔丁酯)(50/50摩尔比)反应

向100 ml圆底烧瓶中加入聚(降冰片烯甲醇-co-降冰片烯叔丁酯)(2g)和1-金刚烷异氰酸酯(1.4 g)。将固体溶于THF (30 ml)中并将烧瓶装上回流冷凝器、搅拌棒和正氮气入口。将所得透明无色溶液回流5小时。然后将烧瓶冷却至室温，将所得物料在水(200 ml)中沉淀、过滤并真空干燥24小时。产量=2.66 g。

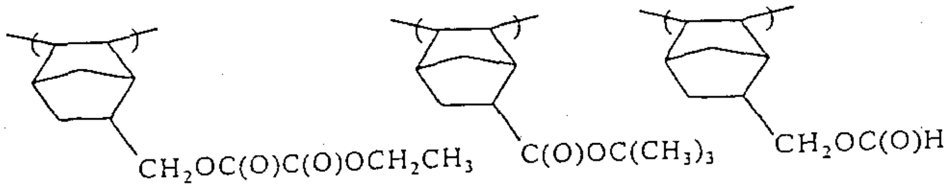
下面的实施例说明可通过将羧酸侧基后官能化加成到多环主链上

改进很多成像因素。抗蚀剂配料按如下方法配制：将示例性聚合物和光致酸生成剂溶于流延溶剂丙二醇甲基醚乙酸酯(PGMEA)中。将该抗蚀剂配料旋涂于硅片上并在130℃下烘烤1分钟。然后将涂布的硅片在ISI ArF Microstep 0.6 NA中在193 nm下通过双掩模曝光。曝光后将硅片在150℃下第二次烘烤1分钟，并用0.21 N四甲基氢氧化铵(TMAH)溶液显影20秒。

实施例36

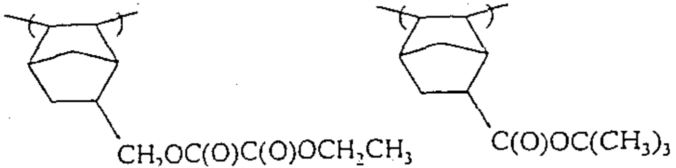
按上述方法制备抗蚀剂组合物和涂布硅片，不同的是无羧酸部分的共聚物的第一次烘烤温度为150℃。将成像和显影的含通过后官能化引入的羧酸部分的光刻胶聚合物的SEM显微照片与无含羧酸部分的光刻胶聚合物的SEM显微照片对比。该含羧酸的聚合物为实施例20中获得的三元共聚物，该聚合物含具有摩尔百分比为50/40/10的草酸酯/叔丁基酯/酸侧基的重复单元。该三元共聚物表示如下：

含草酸酯/叔丁基酯/羧酸的三元共聚物50/40/10



该无羧酸官能团的聚合物为含具有草酸酯/叔丁基酯(摩尔百分比50/50)侧基的重复单元的共聚物。该共聚物表示如下：

草酸酯/叔丁基酯共聚物50/50

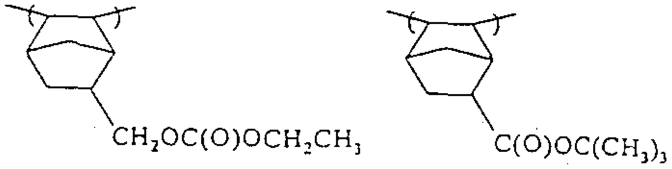


如图1所示，具有0.15μm特征尺寸的成像50/40/10抗蚀三元共聚物显示清晰显影和非常高的分辨率。如图2所示，在高分辨对比（sharp contrast）中，50/50共聚物在相对较高的0.3 μm特征尺寸下显示在大块曝光区域中具有可见浮渣的非常粗糙的显影.

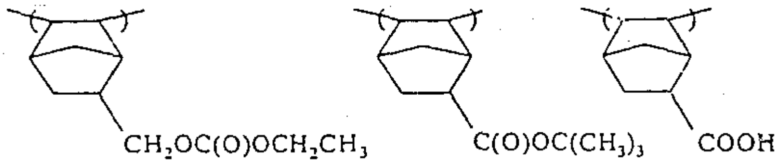
实施例37

本实施例中，将不含具有碳酸酯侧基和叔丁基酯侧基（摩尔百分比50/50）的含羧酸官能团的重复单元的共聚物与含具有摩尔百分比50/40/20和40/40/20的碳酸酯/叔丁基酯/羧酸侧基的重复单元的三元共聚物对比。按如下方法进行聚合物的成像实验和接触角测量。这些聚合物表示如下：

碳酸酯/叔丁基酯共聚物50/50



含碳酸酯/叔丁基酯/羧酸的三元共聚物50/40/10和40/40/20



通过将羧酸官能团后官能化引入聚合物主链中，可控制聚合物的溶解性和亲水性。测量各聚合物表面与水滴的接触角并记录在下表中。该接触角是聚合物亲水性的良好指标。

按如下方法测量接触角：

将聚合物溶于PGMEA中，然后通过0.45 μm Teflon®膜过滤。将过滤溶液旋涂于清洁的硅片上并在140℃下烘烤2分钟使薄膜干燥。

将涂布的硅片放在AST Products VCA图像接触角测角仪上，该接触角测角仪用于测量水滴轮廓与聚合物薄膜表面的相切角。将纯水（2 μ l）用高精确注射泵注射到涂布硅片的表面上。在2或3秒内测量放置于涂布硅片表面上的水滴接触角。对各样品进行重复试验以确保精度。

聚合物组成 碳酸酯/叔丁酯/酸	含酸官能团的 重复单元的mol%	接触角	聚合物 实施例
50/50/0	0	78°	---
50/40/10	10	74°	22
40/40/20	20	69°	23

该接触角与在平版印刷加工期间观察到的极大增强润湿性非常相关。接触角越小，聚合物的亲水性越好。

将这些聚合物配制为抗蚀组合物并按上述方法成像。成像实验的结果证明后官能化引入羧酸官能团对平版印刷性能具有很大影响。50/50共聚物（无羧酸官能团）显示高浮渣含量、粘附损失和不良成像。不能获得低于.45 μm的影像（图中未包括）。加入含羧酸部分（即实施例22的50/40/10聚合物），可以显著降低特征尺寸。图3和4分别给出实施例22的聚合物的1:1间距 0.15 μm和2:1间距 0.12 μm影像的SEM显微照片。间距(pitch)为特征线和特征线之间的间隔与特征线宽度之间的比例。正如在这些图中说明的，印刷了良好限定的清晰影像。

通过加入更多的含羧酸部分（即实施例23的40/40/20聚合物），成像进一步改进了。如图5所示（在1:1间距下的0.16 μm特征尺寸），特征轮廓变得更突出，且特征底部更清晰（很少浮渣）。图6（在3:1间距下的0.10 μm特征尺寸）证明容易印制更小的特征。

这些实施例说明通过后官能化引入含羧酸部分带来亲水性的增加，导致影像质量（特征尺寸和图形美观性）大大提高。

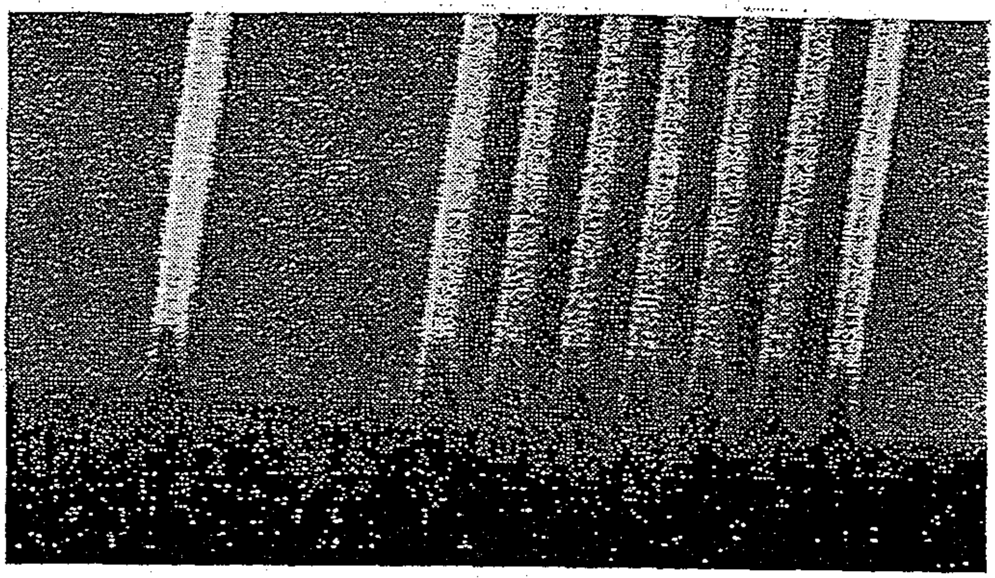


图 1

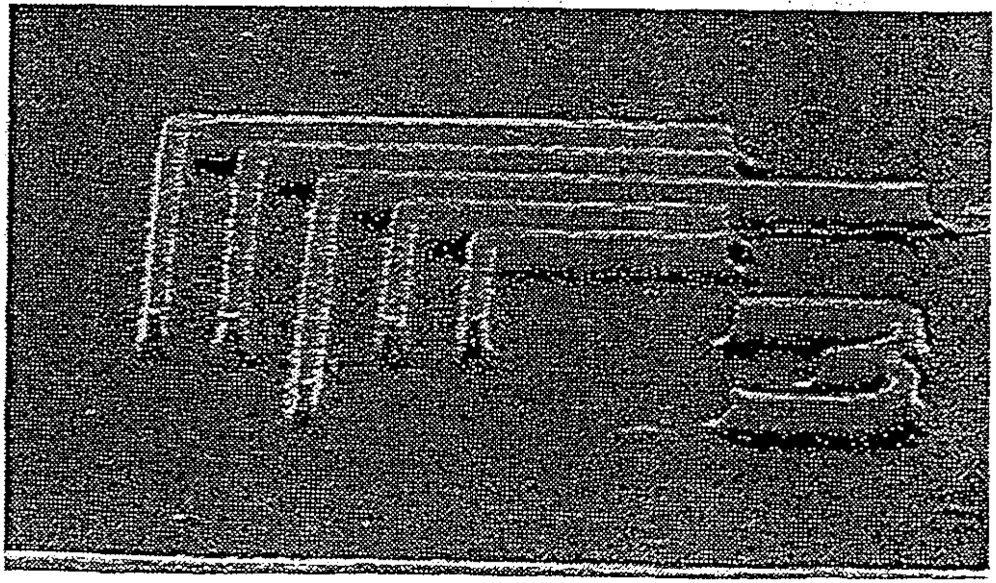


图 2

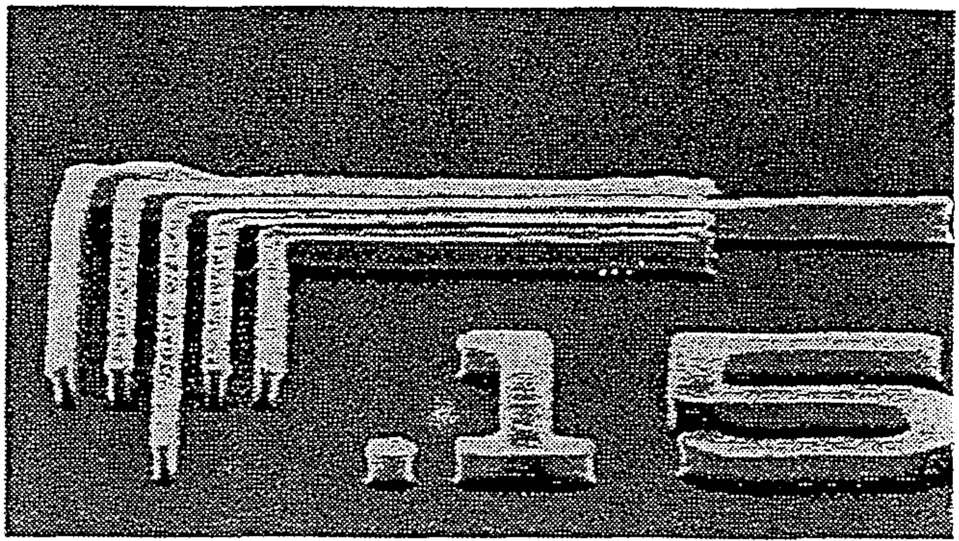


图 3

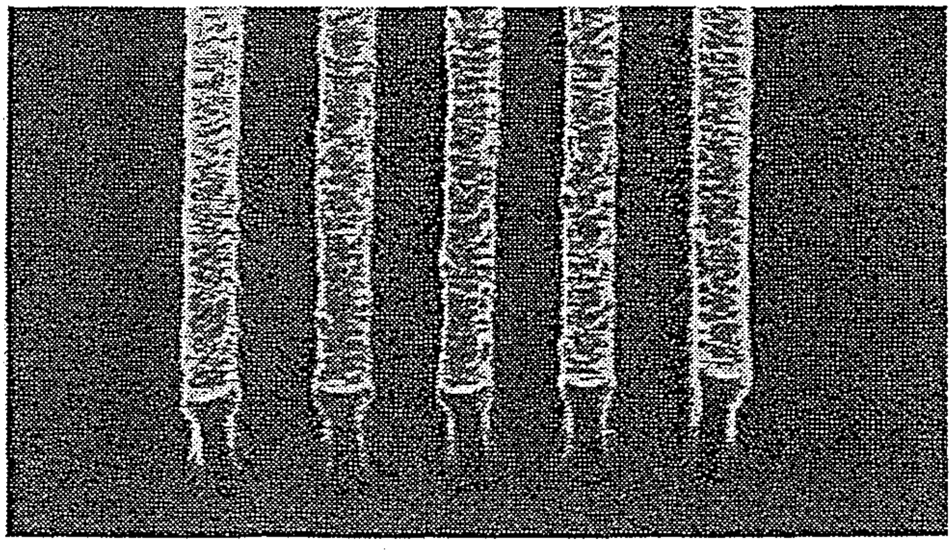


图 4

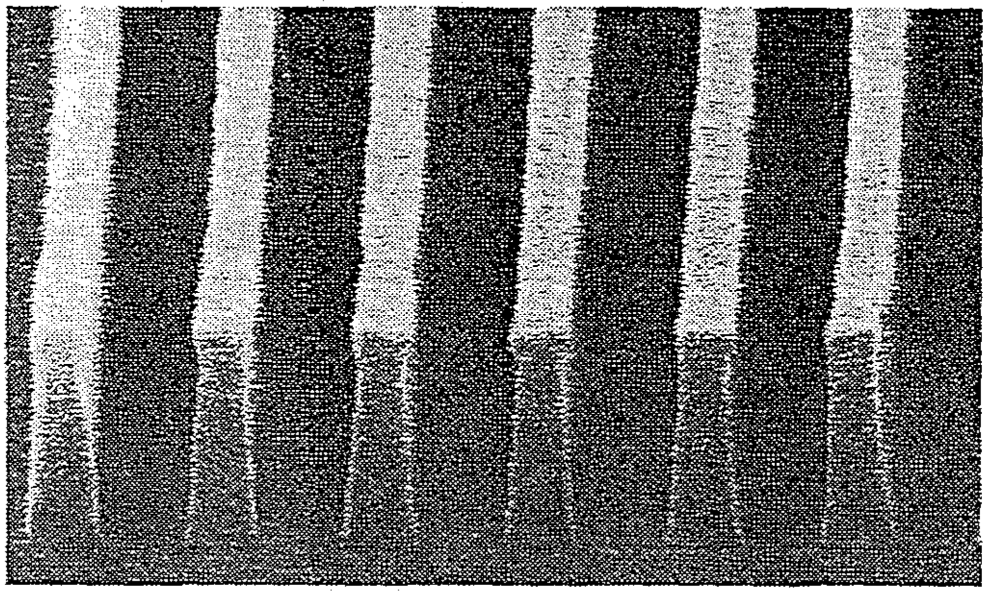


图 5

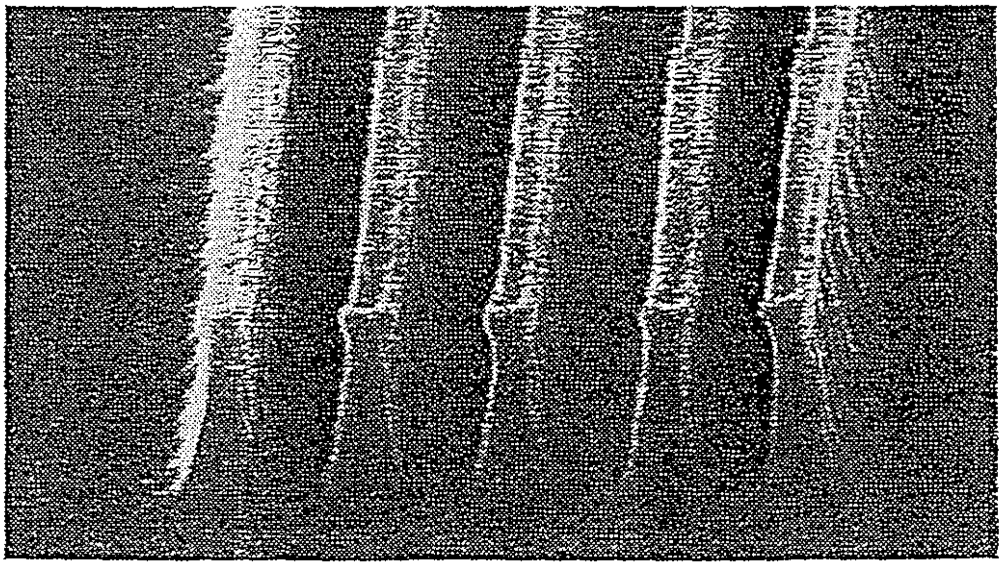


图 6