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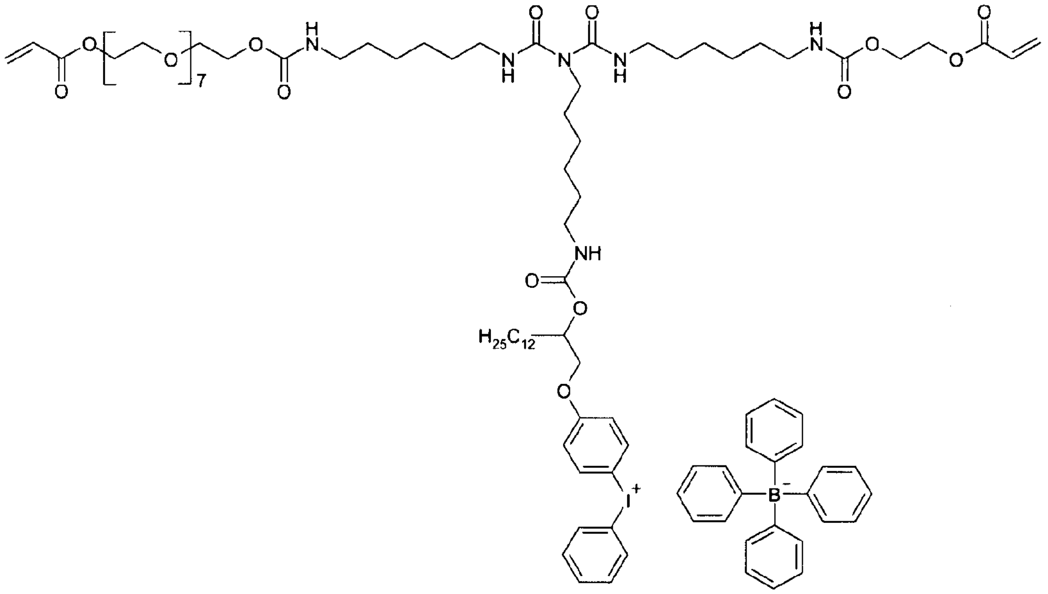
(54) Title: NEW MATERIALS FOR LITHOGRAPHIC PLATES COATINGS, LITHOGRAPHIC PLATES AND COATINGS CONTAINING SAME, METHODS OF PREPARATION AND USE



(57) Abstract: This invention relates to iodonium salts, acetal copolymers and polymer binders comprising functional groups capable of undergoing cationic or radical polymerization, their method of preparation and their use in the preparation of coatings. This invention also relates to coating solutions and coatings containing the iodonium salts, acetal copolymers and/or polymer binders and to negative working lithographic printing plates comprising these coatings.

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TITLE OF THE INVENTION

[0001] NEW MATERIALS FOR LITHOGRAPHIC PLATES COATINGS, LITHOGRAPHIC PLATES AND COATINGS CONTAINING SAME, METHODS OF PREPARATION AND USE

FIELD OF THE INVENTION

[0002] This invention relates to novel materials useful for lithographic plates coatings and to plates, coatings and coating solutions containing these materials. More specifically, these new materials and coating solutions are useful in the preparation of coatings for lithographic offset printing plates for direct digital imaging by near-infrared laser radiation.

BACKGROUND OF THE INVENTION

[0003] On-press developable negative-working lithographic offset printing plates are known in the prior art. Fox example, US patent No. 5,569,573 teaches lithographic printing plates comprising a laser imaging layer containing microencapsulated oleophilic materials in hydrophilic polymer binders. EP 0 770 495 A1 teaches lithographic printing plates comprising near infrared absorption materials, polymer binders and thermoplastic particles capable of coalescing under heat. US patent No. 6,983,694 teach on-press developable negative-working offset printing plates coated with near infrared sensitive coating compositions comprising thermoplastic polymer particles, such as polystyrene or poly(acrylonitrile-co-styrene) particles, non-reactive hydrophilic polymer binder and near infrared absorption dyes.

[0004] Also, US patent No. 6,262,740 teaches negative-working offset printing plates coated with near infrared sensitive coating compositions containing methoxymethacrylamide copolymers, phenolic resins, iodonium salts and near infrared absorption dyes. US patents No. 6,124,425 and 6,177,182 teach on-press developable negative-working offset printing plates coated with thermally near-infrared absorbing polymers, which undergo cross-linking reactions via cationic polymerization upon exposure to near infrared radiation. The near infrared chromophoric moieties are functionalized to the polymeric backbone via ether and ammonium bonds. US Patent No. 6,960,422 teaches negative-working offset printing plates, which contain a near infrared sensitive base-coat compositions comprising molecular near infrared dyes, radical generators, radical polymerizable urethane compounds, reactive polymer binders and other additives.

[0005] Moreover, US Patent No. 6,969,575 and 7,001,704 teach on-press developable negative-working offset printing plates having an image-forming layer, which comprise near infrared absorbing microcapsules and acid generator compound. US patent No. 6,582,882 and co-pending US patent applications Ser. No. 10/066,874; 10/119,454 and 2005/0123853 teach on-press developable negative-working offset printing plates, which are coated with thermally imageable compositions containing polymer binders, initiator systems and polymerizable components. The described polymer binders are copolymers having non-reactive polyethylene oxide and polypropylene block, or graft copolymers having non-reactive polyethylene oxide side chains co-polymerized with acrylonitrile, styrene and other monomers. The polymerizable components are viscous liquid oligomers containing multiple acrylic functional groups. The initiator system contains near infrared absorption dyes and radical producing compounds, such as triazine and iodonium salts.

[0006] All of these coating compositions and printing plates show some disadvantages such as having a tacky surface which causes difficulties for handling and storage, exhibiting phase separation and/or surface crystallization, being difficult to prepare, requiring high laser power to achieve imaging, having poor substrate adhesion and consequently failing to provide sufficient run length on press, not being developable on-press, exhibiting poor scratching resistance, requiring an over-coating layer and/or a special substrate surface treatment and being expensive to manufacture.

[0007] There thus remains a need for new materials and new coatings for lithographic plates that would overcome some or all of the drawbacks of the prior art.

SUMMARY OF THE INVENTION

[0008] This invention relates to iodonium salts, acetal copolymers and polymer binders, each comprising at least one functional group capable of undergoing cationic or radical polymerization

[0009] This invention further relates to the method for preparing the iodonium salts, acetal copolymers and polymer binders of the invention. More specifically, one such method for preparing an iodonium salt of the invention comprises attaching a pendant group to an iodonium salt, wherein the pendant group is obtained by reacting a mono-isocyanate, a di-isocyanate or a poly-isocyanate with an amine or an alcohol, which is terminated by one or more groups each independently selected from acrylate, methacrylate and vinyl-ether.

[0010] The present invention further relates to the use of the iodonium salts, acetal copolymers and polymer binders of the invention or a mixture thereof in the preparation of coating solutions and to the coatings produced using these solutions.

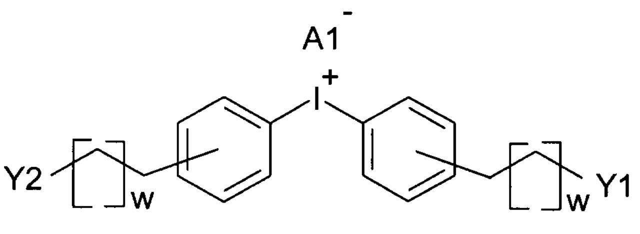
[0011] The invention also relates to coating solutions and to negative working lithographic printing plate comprising the coatings and/or the iodonium salts, acetal copolymers and polymer binders of the invention.

Thermally Reactive Iodonium salts

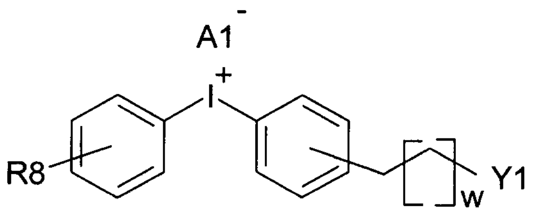
[0012] The present invention relates to iodonium salt comprising a positively charged iodine atom to which two aryl rings are attached, and a negatively charged counter ion. When exposed to near infrared radiation or heat, these salts are radical and acid generators.

[0013] The iodonium salts of the present invention comprise one or more functional groups that can undergo radical and/or cationic polymerization. Upon exposure to heat, the iodonium salt will generate radicals and acid, which will initiate the radical or cationic polymerization of these functional groups. This will contribute to the formation of a network within the irradiated area of the coating.

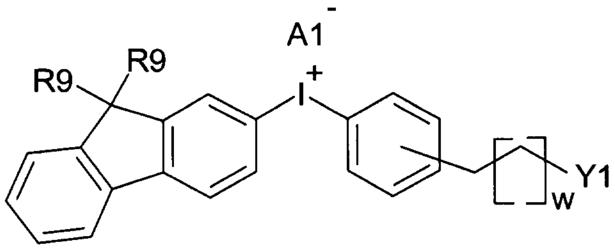
[0014] More specifically, the iodonium salts of the invention may contain radical polymerizable groups, such as acrylate, methacrylate and vinyl ether. These radical polymerizable groups may be pendanted to the aryl rings of the salt via urethane and/or urea bonds. These salts may have the following general structures:



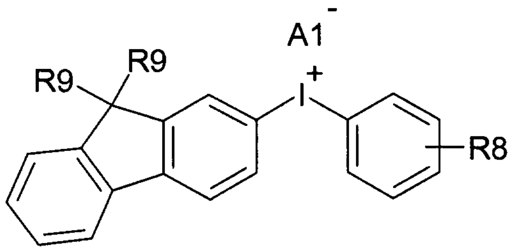
Iodonium I



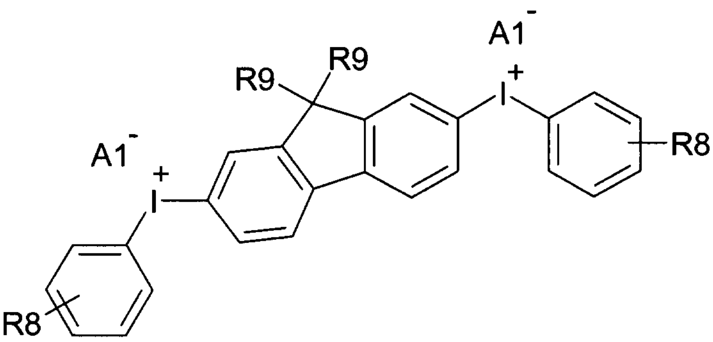
Iodonium II



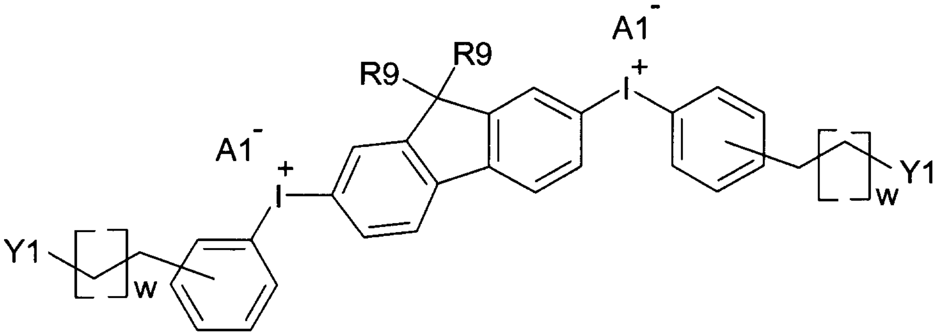
Iodonium III



Iodonium IV



Iodonium V



Iodonium VI

wherein:

- A1 represents an anionic counter ion selected from tosylate, triflate, hexafluoroantimonate, tetrafluoroborate, tetraphenylborate and triphenyl-n-alkylborate;
- w represents the number of repeat unit and may vary between 0 and 18;
- R8 and R9 independently represent hydrogen, linear or branched C1 – C18 alkyl, alkyl oxy, poly(ethylene oxide), poly(propylene oxide) and may comprise

acrylate, methacrylate and vinyl ether terminated groups (In the case of Iodoniums IV and V, either R8, R9 or both R8 and R9 do comprise such acrylate, methacrylate and vinyl ether terminated groups); and

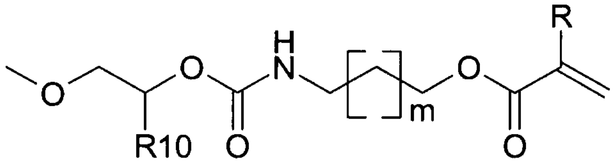
- Y1 and Y2 independently represent urethane and/or urea containing compounds, which comprise single or multiple polymerizable functional groups, such as acrylate, methacrylate or vinyl ether.

[0015] In a more specific embodiment, Y1 and/or Y2 may be obtained by reacting a mono-isocyanate, di-isocyanate and/or poly-isocyanate with an amine or an alcohol comprising single or multiple acrylate, methacrylate and/or vinyl-ether terminated groups. These isocyanate compounds may be Desmodur™ N100, Desmodur™ N3300, Desmodur™ CB 75N, Desmodur™ I, Desmodur™ W, Desmodur™ M, Desmodur™ H and Desmodur™ TD 80, which are sold by Bayer Canada.

[0016] In a specific embodiment, the alcohol comprises multiple acrylate terminated groups. Such alcohol may be are obtained from Sartomer. This alcohol may be pentaerylthritol triacrylate (Trade-name SR 444) and dipentaerylthritol pentaacrylate (Trade-name SR399).

[0017] In another specific embodiment, the alcohol comprises single acrylate and methacrylate compounds and may be obtained from Sigma-Aldrich Canada. The alcohol may be 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylacrylate, 4-hydroxybutylmethacrylate, 6-hydroxyhexylacrylate, 6-hydroxyhexylmethacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(propylene glycol) acrylate and poly(propylene glycol) methacrylate.

[0018] Y1 and Y2 may have the following chemical structures:



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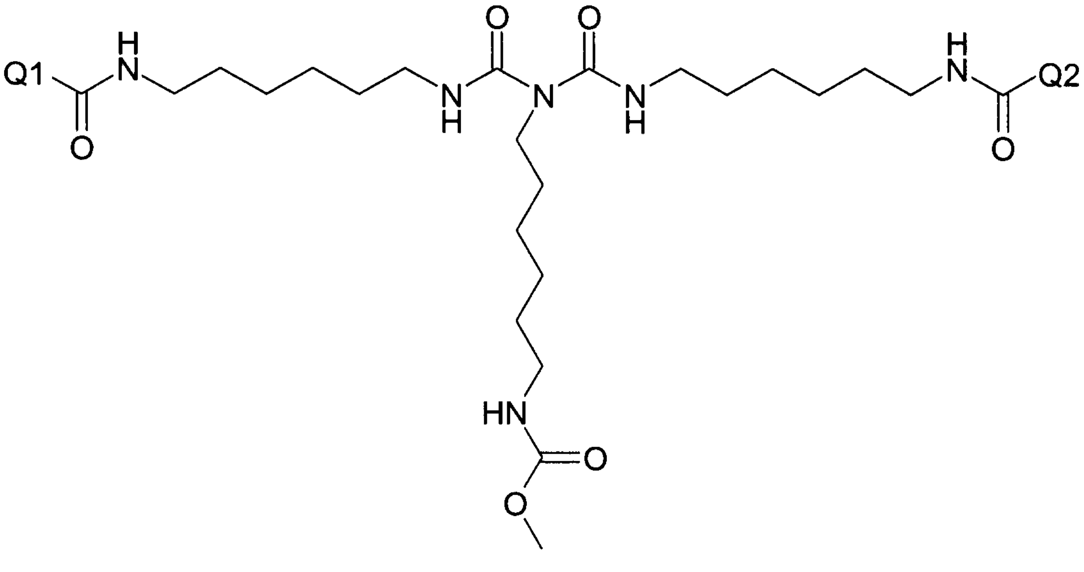
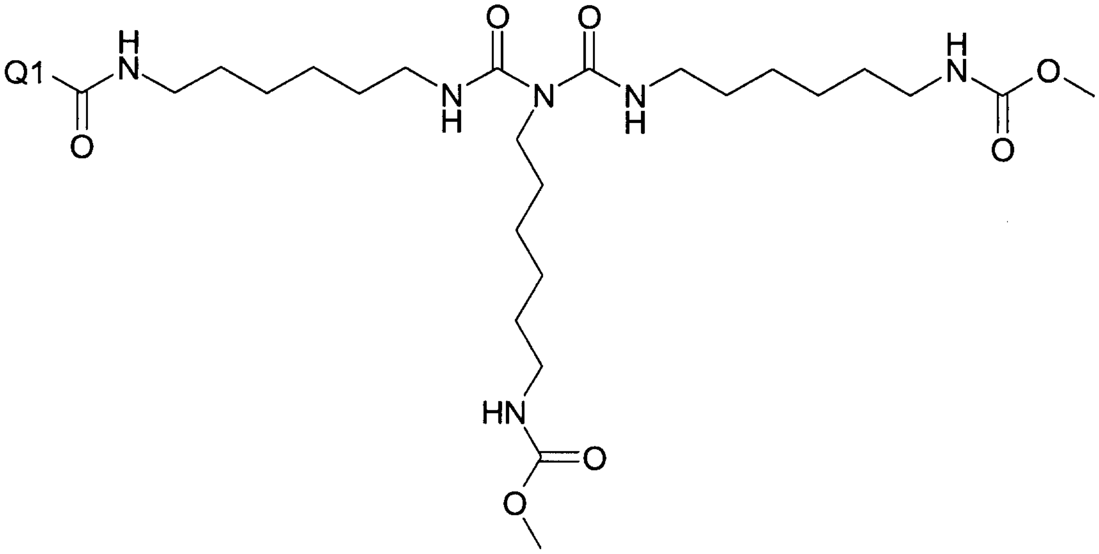


, or



wherein:

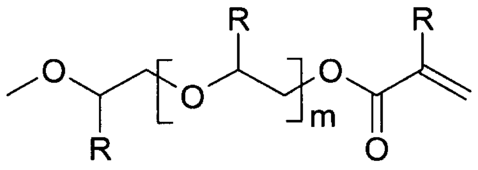
m varies between 1 and 18,

R is hydrogen or methyl

R10 is hydrogen or a linear or branched C1-C18 alkyl chain; and

Q1 and **Q2** independently represent an end compound comprising single or multiple polymerizable functional groups.

[0019] More specifically, Q1 and Q2 may independently have any of the following structures:



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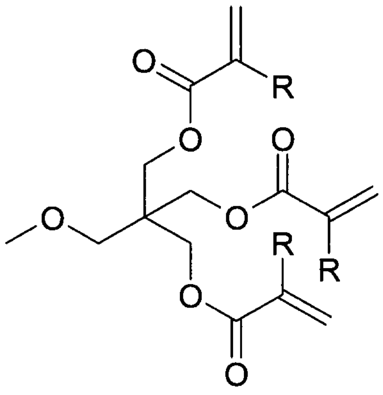
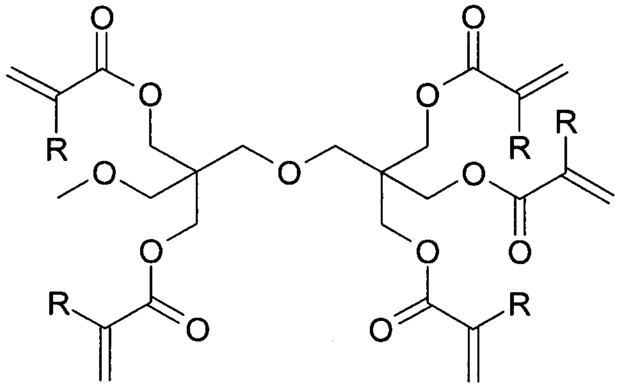


, or



wherein R is hydrogen or methyl.

[0020] The synthesis of urethane containing iodonium salts having no reactive (polymerizable) functional groups can be seen in US Patent No. 6,380,277, which is incorporated herein as reference.

[0021] The iodonium salt of the present invention may be used for the preparation of coating solutions and coatings. Such coating may comprise from about 5 to about 60 % by solid weight of the iodonium. The coatings are usually prepared by depositing a coating solution comprising the iodonium salt onto a substrate. These solutions comprise a solvent or a mixture of solvent allowing the formation of the coating. Any solvent known to the person of skill in the art to be appropriate for this purpose can be used. Examples of such solvents include n-propanol, water and other similar solvents.

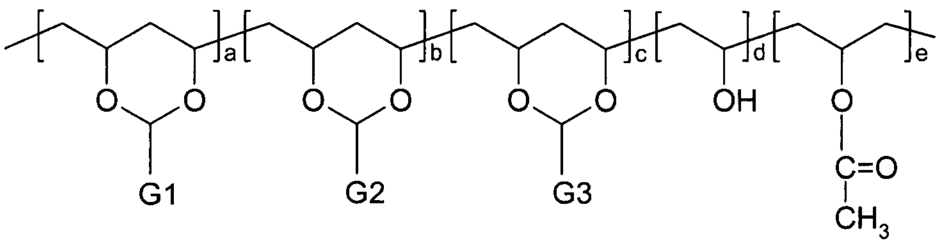
[0022] In a specific embodiment, the coating/coating solution of the present invention comprises a mixture of iodonium salts, which may ease the manufacturing process.

Near infrared absorbing dyes

[0023] The coating/coating solution of the present invention may also comprise a near infrared absorbing dye which produces heat upon exposure to near infrared radiation. More specifically, this near infrared absorbing dye may be a molecular dye, a dimeric dye, a dendrimeric dye or a polymeric dye. In a specific embodiment, this dye is an acetal copolymer.

[0024] This molecular dye, and more particularly this acetal copolymer, may have attached thereto a functional group capable of undergoing cationic or radical polymerization. Therefore, when the iodonium salt produces acid/radicals, this functional group will react with other such functional groups present in the coating, for example that of the iodonium salt, to produce a chemical link, and contribute to the formation of a network within the irradiated area of the coating.

[0025] More specifically, the near infrared absorbing acetal copolymers may have a molecular weight greater than about 2,000 g/mol and may either be soluble in organic solvents or in aqueous solutions. Furthermore, they may have the following general structure:

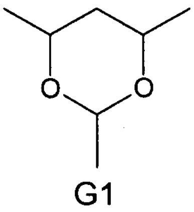


Formula 1

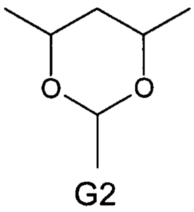
wherein:

- G1 represents an optional processing segment that provides solubility in organic solvents such as alcohol, ketone, and ester;
- G2 represents an optional thermal reactive segment;
- G3 represents a radiation-absorbing segment that exhibits one or more strong absorption bands between 700 and 1100 nm. Optionally, this segment may also exhibit strong absorption bands between 400 and 700 nm;
- a, b, c, d and e are molar ratios that can vary from 0.01 to 0.99; and

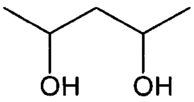
- when the optional G1 and/or G2 segments are not present,



and/or



, respectively are replaced by

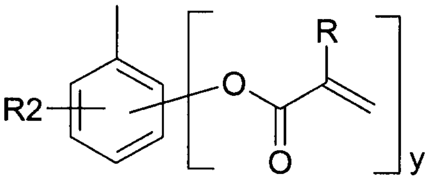


.

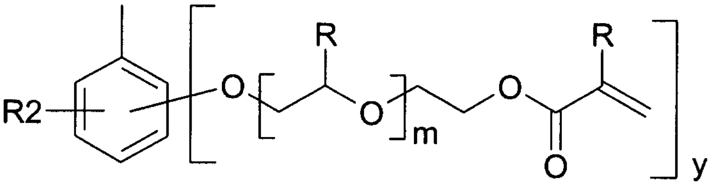
[0026] More specifically, the G1 processing segment of this invention may be a linear or branched alkyl or aryl compound containing cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide, methylbenzylsufonyl-carbamate or carboxylic acid and phosphoric acid functional groups.

[0027] The G2 thermal reactive segment of this invention may be a linear or branched alkyl or aryl compound and may contain a functional group capable of undergoing radical and/or cationic polymerization, such as acrylate, methacrylate, and vinyl ether.

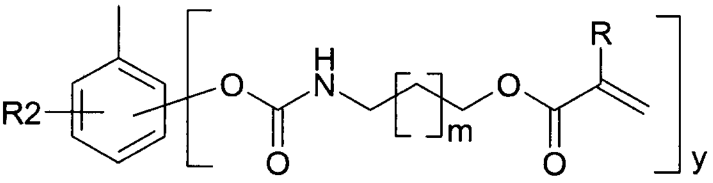
[0028] The G2 thermal reactive segment may have the following structures:



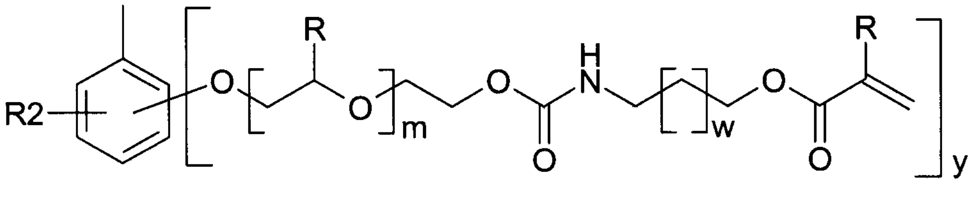
Formula 2



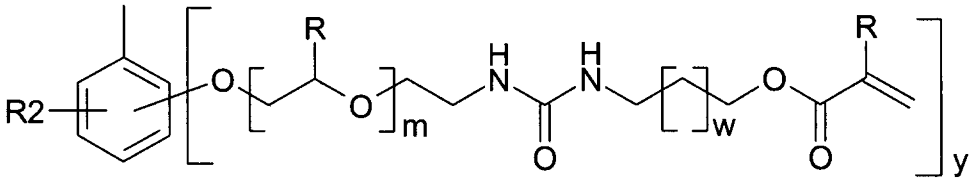
Formula 3



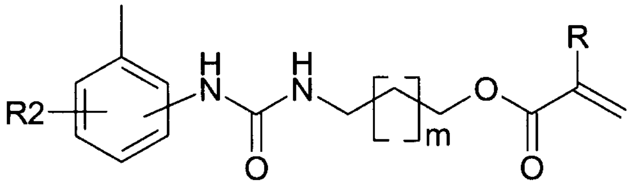
Formula 4



Formula 5



Formula 6



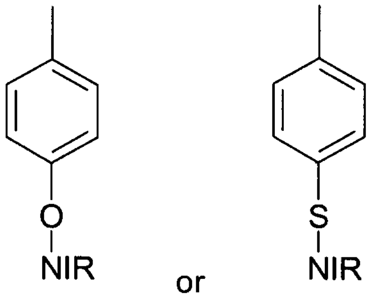
Formula 7

wherein:

- R is hydrogen or methyl;
- R2 is C1 – C8 alkyl or alkoxy;
- m and w represent the number of repeat and may vary between 0 and 50;
- y is 1 or 2.

[0029] In another specific embodiment, the G2 segments may have pendant groups to those illustrated in formulas 2 to 7, but terminated with vinyl ether, alkoxymethyl acrylamide or alkoxy methacrylamide functional groups.

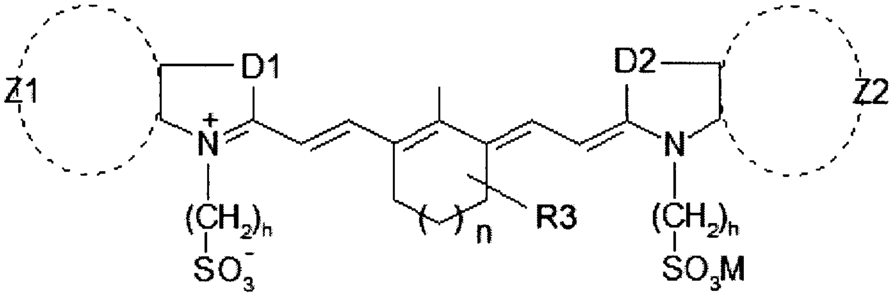
[0030] The G3 segment may be similar to that described in US Provisional Patent No. 60/722,977, which is incorporated herein as reference. More specifically, the G3 segment may have the following structures:



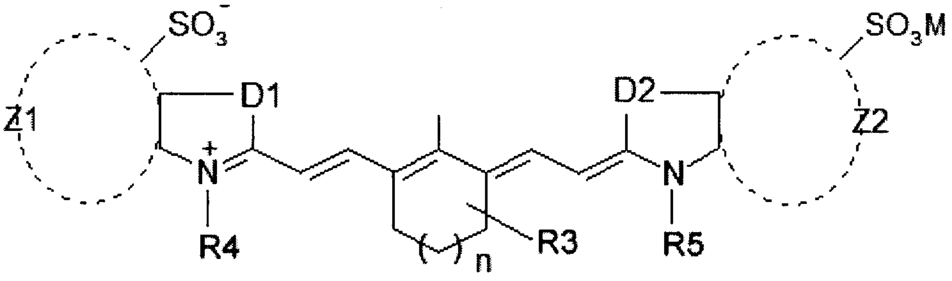
wherein NIR is a near-infrared absorbing chromophore that exhibits one or more strong absorption peaks between 700 and 1100 nm and may optionally exhibit one or more strong absorption peaks between 400 and 700 nm.

[0031] The acetal polymer of the invention may also comprise different G3 segments comprising different near-infrared absorbing chromophores.

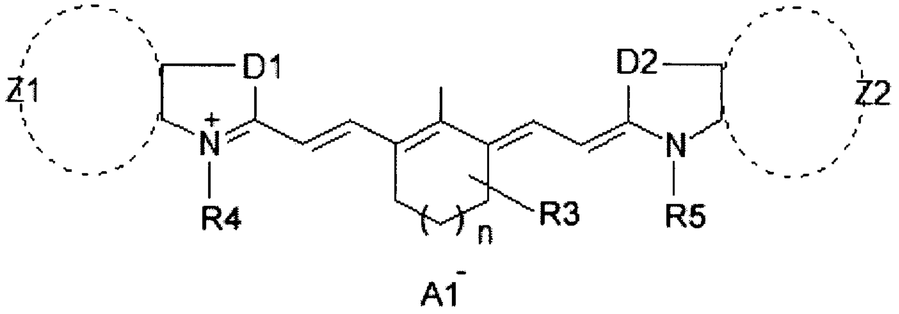
[0032] The near-infrared absorbing chromophores (NIR chromophores) may be near infrared absorbing organic compounds containing cyanine and/or arylimine functional groups. These chromophores may have the following structures:



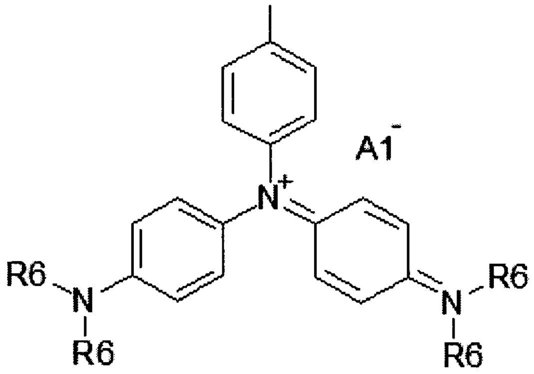
NIR Chromophore I



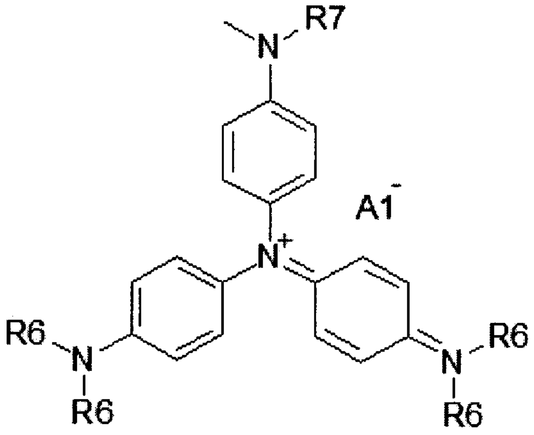
NIR Chromophore II



NIR Chromophore III



NIR Chromophore IV



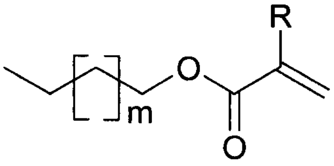
NIR Chromophore V

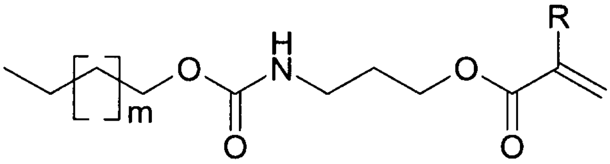
wherein:

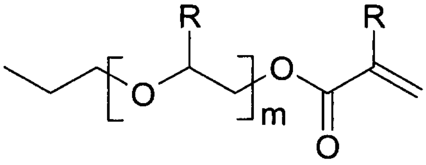
- D1 and D2 are identical or different and represent -O-, -S-, -Se-, -CH = CH-, and -C(CH3)$_2$;
- Z1 and Z2 are identical or different and represent one or more fused substituted or unsubstituted aromatic rings, such as phenyl and naphthyl;
- h represents integer number from 2 to 8;
- n represents 0 or 1;
- M represents hydrogen or a cationic counter ion selected from Na, K, and tetraalkylammonium salts.

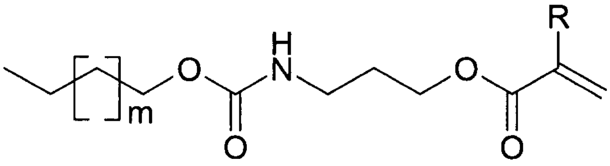
- A1 represents an anionic counter ion selected from bromide, chloride, iodide, tosylate, triflate, trifluoromethane carbonate, dodecyl benzosylfonate and tetrafluoroborate, tetraphenylborate and triphenyl-n-butylborate.
- R3 and R7 represent hydrogen or alkyl; and
- R4, R5 and R6 are identical or different and represent alkyl, aryl alkyl, hydroxy alkyl, amino alkyl, carboxy alkyl, sulfo alkyl.

[0033] In a specific embodiment, R4, R5 and R6 may represent a polymerizable substituents having the following structure:









wherein:

- m is a number of $-CH_2-$ on the alkyl chain and may vary between 0 and 50; and
- R is hydrogen or methyl.

[0034] The near infrared absorbing acetal copolymers may be used in the coating of the present invention in quantities ranging from about 5 to 50 % by solid weight.

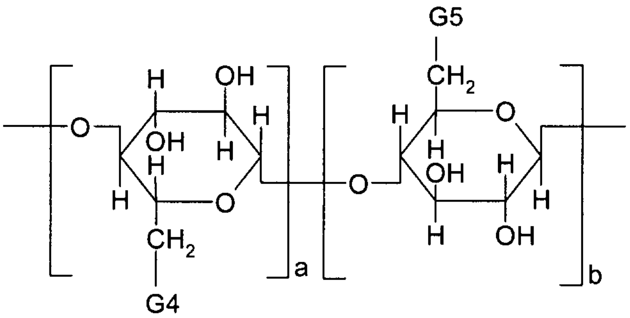
Polymer binders

[0035] The coating/coating solution of the present invention may also comprise a polymer binder. This polymer binder may be used in the coating in quantities ranging from about 1 to about 50 % by solid weight.

[0036] More specifically, the polymer binders of this invention may be polymers, copolymers or dendrimers, which may comprise functional group(s) which can undergo radical and/or cationic polymerization. Therefore, when the iodonium salt produces acid/radicals, these functional groups will react with other such functional groups present in the coating, for example that of the iodonium salt and the dye (if present), to produce chemical links, and contribute to the formation of a network within the coating.

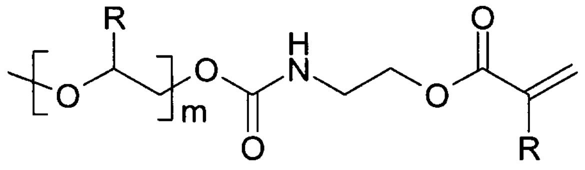
[0037] Specifically, these functional groups may be acrylate, methacrylate, and vinyl ether. More specifically, these functional groups may be cation reactive functional groups such as hydroxy, N-methoxymethylacrylamide and N-methoxymethylmethacrylamide.

[0038] The polymer binders of the invention may be solvent- and/or water-soluble cellulose ethers comprising a functional group which can undergo radical and/or cationic polymerization. This cellulose ether may be obtained by reacting of 2-isocyanto-ethyl methacrylate with the hydroxymethyl, hydroxyethyl and hydroxypropyl group on the cellulose backbone. The cellulose ether of the invention may have the following structure:

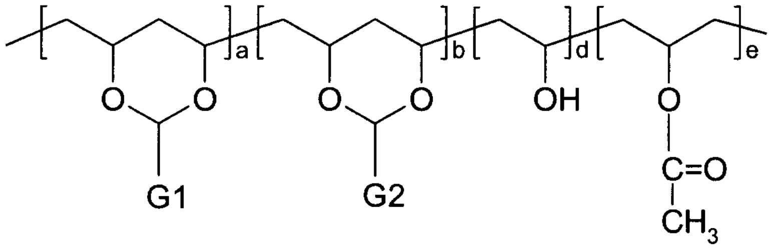


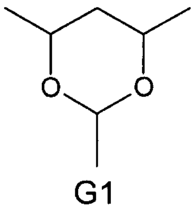
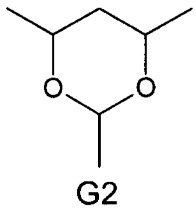
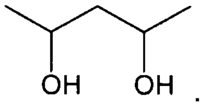
wherein:

- G4 is hydroxy, hydroxyethyl and hydroxypropyl.
- G5 is the functional group which can undergo radioal and/or cationic polymerization.

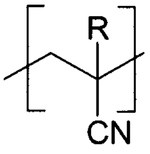
[0039] More specifically, the G5 groups may have the following structure  wherein m is 0 or 1 and R is hydrogen or methyl.

[0040] The polymer binder of the invention may also be an acetal copolymer which does not absorb near infrared radiation. More precisely, the acetal copolymers of this invention may have the following general structure:



wherein G1, G2, a, b, d and e are similar to those defined in Formula 1 as above and wherein when the optional G1 and/or G2 segments are not present,  and/or  , respectively, are replaced by  .

[0041] The polymer binders of the invention may also be copolymers comprising a functional group which can undergo radical and/or cationic polymerization. Such copolymers can be obtained from acrylonitrile, styrene, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate and methoxymethylmethacrylamide monomers. More precisely, the copolymers of the invention may be obtained by copolymerizating (1) at least one non reactive segment selected from: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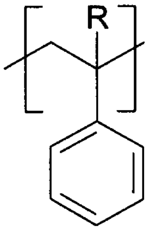
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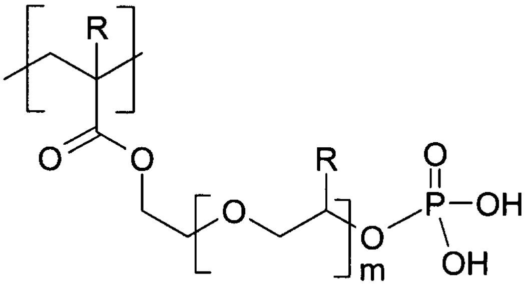
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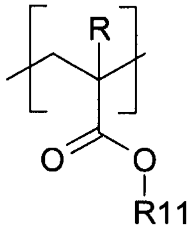
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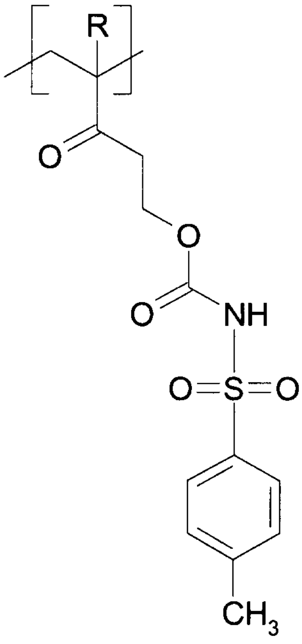
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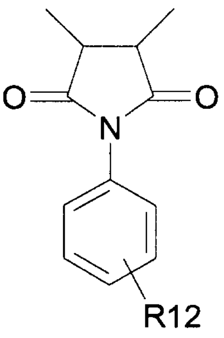
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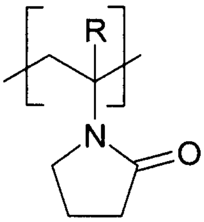
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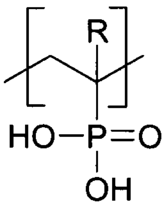
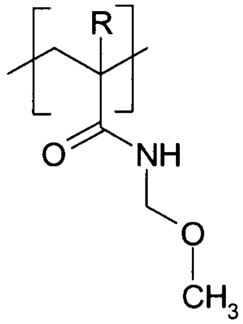


and (2) at least one reactive segment selected from: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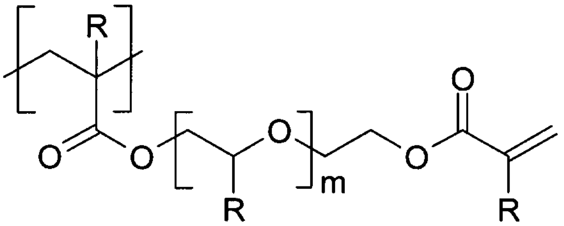
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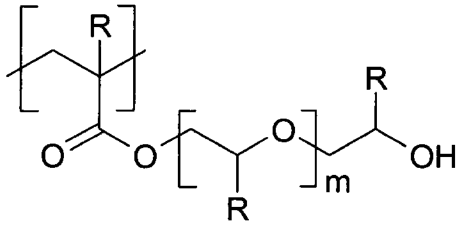
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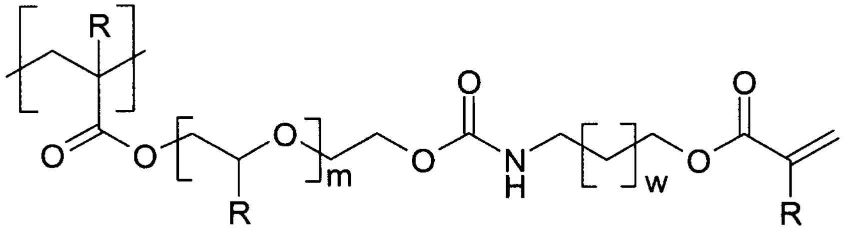
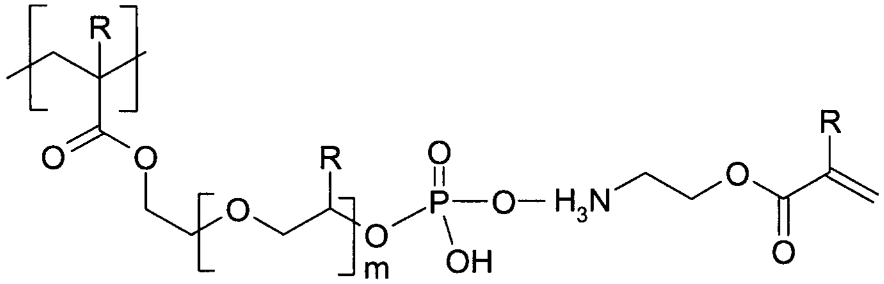


, or



wherein:

- m and w are represent the number of repeat unit and may vary between 0 and 50;
- R is hydrogen or methyl;
- R11 is linear and branched alkyl chain; and
- R12 is alkyl, hydroxyl and carboxylic acid.

[0042] The acetal copolymer of the present invention may be used in the preparation of a coating/coating solution. The coating/coating solution may also comprise the iodonium salt of the present invention and a polymer binder in the above mentioned quantities.

[0043] The polymer binder of the present invention may be used in the preparation of a coating/coating solution. The coating/coating solution may also comprise the iodonium salt of the present invention and a near-infrared absorbing moiety in the above mentioned quantities.

Colorants and stabilizers

[0044] The coatings/coating solutions of the invention may also comprise colorants to provide good image printout after laser imaging. These colorants of this invention may be the derivatives of triarylpyridine, xanthene and isobenzofuranone. These color-generating compounds may be colorless and then become colored in the presence of free radical or acid. More specifically, these compounds may be:

- 3',6'-bis[N-[2-chlorophenyl]-N-methylamino]spiro[2-butyl-1,1-dioxo[1,2-

benz isothiazole-3(3H),9'-(9H)xanthene]](prepared by the method of US Patent No. 4,345,017);

- 3',6'-bis[N-[2-[methanesulfonyl]phenyl]-N-methylamino]spiro[2-butyl-1,1-dioxo[1,2-benzisothiazole-3(3H),9'-(9H)xanthene]](prepared by the method of US Patent No. 4,345,017);
- 9-Diethylamino[spiro[12H-benzo(a)xanthene-12,1'(3'H)-isobenzofuran)-3'-one] (available from BF Goodrich, Canada);
- 2'-di(phenylmethyl)amino-6'-[diethylamino]spiro[isobenzofuran-1(3H),9'-(9H)-xanthen]-3-one (available from BF Goodrich, Canada);
- 3-[butyl-2-methylindol-3-yl]-3-[1-octyl-2-methylindol-3-yl]-1-(3H)-isobenzo furanone (available from BF Goodrich, Canada);
- 6-[dimethylamino]-3,3-bis[4-dimethylamino]-phenyl-(3H)-isobenzofuranone (available from BF Goodrich, Canada);
- 2-[2-Octyloxyphenyl]4-[4-dimethylaminophenyl]-6-phenylpyridine (available from BF Goodrich, Canada); or
- Leuco lactone dyes, such as Blue-63, GN-169 and Red-40 (available from Yamamoto Chemicals Inc., Japan).

[0045] The colorants may be used in the coatings of the present invention in quantities ranging from 0.5 to 5 % by solid weight.

[0046] The coatings/coating solutions of the invention may also comprise stabilizers to prolong the shelf-life of the printing plates during storage. These stabilizers may be methoxyphenol, hydroxyphenol, phenothiazine, 3-mercapto triazol or monomethyl ether hydroquinone. These stabilizers may be used in the coatings of the present invention in quantities ranging from 0.5 to 5 % by solid weight.

Negative-working lithographic printing plates

[0047] The coating solutions of the present invention may be used in the preparation of negative-working lithographic printing plates.

[0048] This invention therefore also relates to printing plates containing the iodonium salts, the acetal copolymers and/or the polymer binders of the present invention. These lithographic offset printing plates may be directly imaged with near-infrared laser imaging devices in computer-to-plate and digital offset printing technologies.

[0049] More specifically, such coating solutions may be used in the production of on-press developable negative-working lithographic offset printing plates that comprise single- or multiple-layer coatings deposited on a substrate such as anodized aluminum, plastic films or paper.

[0050] The aluminum substrate may be brushed-grained or electro-grained, then anodized with acidic solutions.

[0051] The anodized aluminum substrate may be coated with a polymeric adhesion-promoting layer. The adhesion-promoting and heat insulating layer may be obtained from water solutions containing poly(acrylic acid), poly(acrylic acid-co-vinylphophoric acid) or polyvinyl phosphoric acid, which are then dried using hot air at about 110°C. The coating weight of the adhesion-promoting layer may be between about 0.1 and about 1.0 g/m^2.

[0052] The thermally reactive coating solutions may be deposited on top of the adhesion-promoting layer and may have a coating weight between about 0.5 and about 2.5 g/m^2.

[0053] Other embodiments and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art.

BRIEF DESCRIPTION OF THE DRAWINGS

[0054] In the appended drawings:

[0055] Figure 1 is the ideal structure of acetal copolymer PVA-01 ;

[0056] Figure 2 is the ideal structure of acetal copolymer PVA-02;

[0057] Figure 3 is the ideal structure of acetal copolymer PVA-03;

[0058] Figure 4 is the ideal structure of acetal copolymer PVA-04;

[0059] Figure 5 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0060] Figure 6 is the possible structure of a specific embodiment of a n iodonium salt of the present invention;

[0061] Figure 7 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0062] Figure 8 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0063] Figure 9 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0064] Figure 10 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0065] Figure 11 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0066] Figure 12 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0067] Figure 13 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0068] Figure 14 is the ideal structure of a specific embodiment of an iodonium salt synthesized from fluorene compound;.

[0069] Figure 15 is the ideal structure of polymer binder RPB-01;

[0070] Figure 16 is the ideal structure of polymer binder RPB-03;

[0071] Figure 17 is the ideal structure of polymer binder RPB-04;

[0072] Figure 18 is the ideal structure of polymer binder RPB-05;

[0073] Figure 19 is the ideal structure of polymer binder RPB-06;

[0074] Figure 20 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0075] Figure 21 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0076] Figure 22 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0077] Figure 23 is the possible structure of a specific embodiment of an iodonium salt of the present invention;

[0078] Figure 24 is the possible structure of a specific embodiment of an iodonium salt of the present invention; and

[0079] Figure 25 is the possible structure of a specific embodiment of an iodonium salt of the present invention.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

[0080] The present invention is illustrated in further details by the following non-limiting examples.

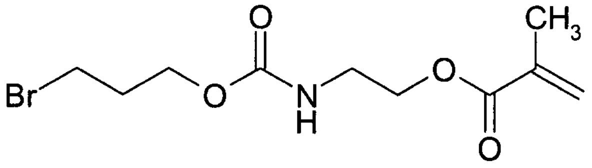
[0081] In these examples, these syntheses were performed in a 4 necks glass reactor equipped with a water condenser, a mechanical stirrer, a dropping funnel and a nitrogen or air gas inlet. The molecular structures of the obtained materials were determined by proton NMR and FTIR spectroscopy. The average molecular weight of the copolymers obtained was determined by size exclusion chromatography (SEC), using N,N-dimethylformamide (DMF) solutions and calibrated with polystyrene standards. The UV-Visible near-infrared spectra of the synthesized polymers were measured in methanol solutions or on the solid films using a UV-VIS spectrophotometer (PerkinElmer, Model Lambda 35).

[0082] Also, the coated plates were imaged using Creo Trendsetter 3244 equipped with 830 nm lasers. The imaged plate was mounted on AB Dick duplicator press using black ink (available from Pacific Inks, Vietnam) and fountain solution containing 3.0 parts of MYLAN-FS100 in 97.0 parts of water (available from MyLan Chemicals Inc., Vietnam).

Synthesis of the reactive near-infrared sensitizing acetal copolymers (dyes):

EXAMPLE 1

[0083] The thermally reactive near-infrared sensitizing acetal copolymer PVA-01 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (100 mmole, available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 1 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. After hydrogen gas was no longer produced from the reaction, 3.0 grams of 3-bromopropyl-methacryloyl-ethyl carbamate (see structure below, available from American Dye Source Inc., Canada) was added into the reaction mixture.



3-bromopropyl-methacryloyl-ethyl carbamate.

[0084] The reaction was continued for 30 minutes, then 20 grams of 2-[2-[2-chloro-3-[[1,3-dihydro-1,1-dimethyl-3-(4-sulfonylbutyl)-2H-benzo[e]indol-2-ylidene]-ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,1-dimethyl-3-(4-sulfonylbutyl)-1H-benzo[e]indolium hydroxy inner salt, sodium salt (13 mmole, available from American Dye Source, Inc.) was slowly added to the flask. The resulting mixture was stirred at 60°C for another 5 hours. The reaction product was precipitated in acetone, filtered and washed copiously with acetone. It was then dried in air until constant weight.

[0085] The UV-Vis-NIR spectrum of the obtained PVA-01 thermally reactive near-infrared absorbing acetal copolymer was recorded in methanol and exhibited a strong absorption band at 803 nm. The ideal structure of the PVA-01 near-infrared absorbing acetal copolymer is shown in Figure 1, wherein a = 6.65%, b= 1.00 %, c= 2.35%, d=88.00% and e = 2.00%.

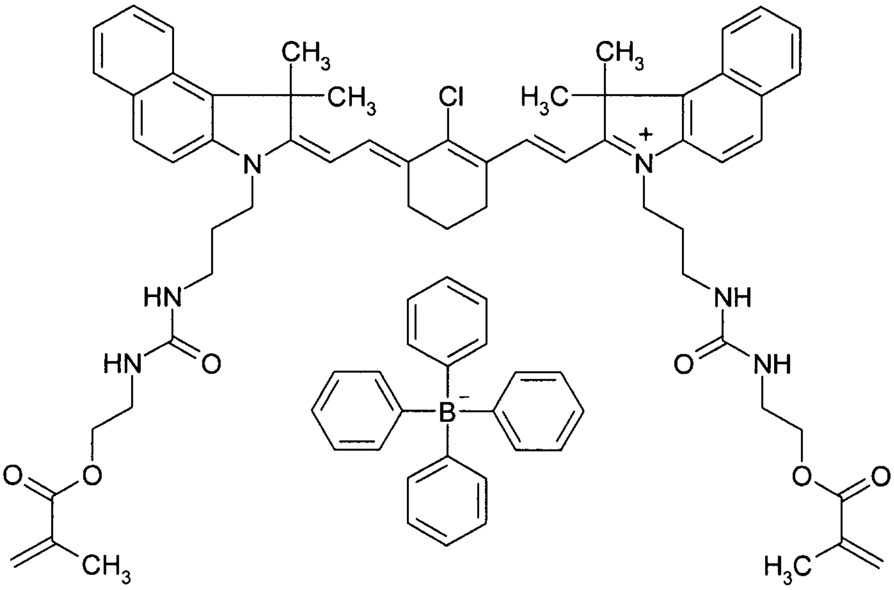
EXAMPLE 2

[0086] The thermally reactive near-infrared absorbing acetal copolymer PVA-01 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (100 mmole, available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 1 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. After hydrogen gas was no longer produced from the reaction, 3.0 grams of 3-bromopropyl-methacryloyl-ethyl carbamate was added into the reaction mixture. The reaction was continued for 30 minutes, then 20 grams of 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethyl-1H-indolium chloride (available from American Dye Source, Inc.) was slowly added to the flask. The resulting mixture was stirred at 60°C for another 3 hours. Then, 5 grams of sodium tetraphenylborate was added into the reaction flask and it continued to stir for additional 2 hours. The reaction product was precipitated in de-ionized water, filtered and washed copiously with water. It was then dried in air until constant weight.

[0087] The UV-Vis-NIR spectrum of the obtained PVA-02 thermally reactive near-infrared absorbing acetal copolymer was recorded on a thin film and exhibited a strong absorption band at 800 nm. The ideal structure of the PVA-02 near-infrared absorbing acetal copolymer is shown in Figure 2, wherein a = 5.15%, b= 1.00%, c= 3.85%, d=88.00% and e = 2.00%.

EXAMPLE 3

[0088] The thermally reactive near-infrared absorbing acetal copolymer, PVA-01, was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 6.1 grams of 4-hydroxybenzaldehyde (available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 0.5 grams of sodium hydride (60 % in mineral oil, After hydrogen gas was no longer produced from the reaction, 10 grams near infrared absorption containing reactive functional groups having the structure shown below (available from American Dye Source, Inc.) was slowly added to the flask.

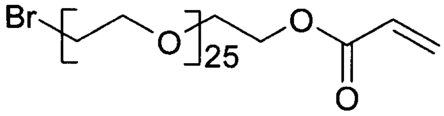


[0089] The resulting mixture was stirred at 50°C for another 5 hours. The reaction product was precipitated in 10 liters of de-ionized water, filtered and washed copiously with water. It was then dried in air until constant weight.

[0090] The UV-Vis-NIR spectrum of the obtained PVA-03 thermally reactive near-infrared absorbing acetal copolymer was recorded on a thin film and exhibited a strong absorption band at 830 nm. The ideal structure of the near infrared absorbing acetal copolymer PVA-03 is shown in Figure 3, wherein a = 3.42 %, c=1.58 %, d= 93.00% and e=2.00%.

EXAMPLE 4

[0091] The thermally reactive near-infrared absorbing acetal copolymer PVA-01 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 1 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. When hydrogen gas was no longer produced from the reaction, 11.0 grams of 10 grams of bromo-terminated poly(ethylene glycol) acrylate (see below structure, available from American Dye Source Inc.) was added into the reaction mixture.



Bromo-terminated poly(ethylene glycol) acrylate

[0092] The reaction was continued for 30 minutes, then 20 grams of 2-[2-[2-chloro-3-[2-(1,3-dihydro-1,3,3-trimethyl-2H-indol-2-ylidene)-ethylidene]-1-cyclohexen-1-yl]ethenyl]-1,3,3-trimethyl-1H-indolium 4-methylbenzene sulfonate (available from American Dye Source, Inc.) was slowly added to the flask. The resulting mixture was stirred at 60°C for another 3 hours. Then, 5 grams of sodium tetraphenylborate was added into the reaction flask and it continued to stir for additional 2 hours. The reaction product was precipitated in de-ionized water, filtered and washed copiously with water. It was then dried in air until constant weight.

[0093] The UV-Vis-NIR spectrum of the obtained PVA-04 thermally reactive near-infrared absorbing acetal copolymer was recorded on a thin film and exhibited a strong absorption band at 800 nm. The ideal structure of the PVA-04 near-infrared absorbing acetal copolymer is shown in Figure 4, wherein a = 5.15%, b= 1.00%, c= 3.85%, d=88.00% and e = 2.00%.

Synthesis of Reactive Iodonium Salts:

[0094] For the ease of manufacturing and cost effectiveness, the iodonium salts containing reactive functional groups may be synthesized and used as a mixture of various salts. Further, this mixture may be used directly without further purification.

EXAMPLE 5

[0095] A mixture of reactive iodonium tetraphenylborate having possible structures as in Figures 5, 6, 7, 8, 9 and 10 was obtained by heating 320 grams of 1,3-dioxolane solution containing 573 grams of Desmodur™ N100 (available from Bayer Canada), 60 grams of 2-hydroxyethylacrylate (available from Sigma-Aldrich, Canada), 245 grams of poly(ethylene glycol) acrylate (Mn ~ 375, available from Sigma-Aldrich, Canada), 500 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a –N=C=O peak at 2274 cm^{-1}. Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the –N=C=O peak at 2274 cm-1 had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 6

[0096] A mixture of reactive iodonium tetraphenylborate having possible structures as in Figures 6, 7 and 8) was obtained by heating 320 grams of anhydrous methyl ethyl ketone solution containing 573 grams of Desmodur™ N100 (available from Lanxess, Canada), 138 grams of 2-hydroxyethylacrylate (available from Sigma-Aldrich, Canada), and 500 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a –N=C=O peak at 2274 cm^{-1}. Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the –N=C=O peak at 2274 cm-1 had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 7

[0097] A mixture of reactive iodonium tetraphenylborate having possible structures as in Figures 8, 9 and 10 was obtained by heating 320 grams of methyl ethyl ketone solution containing 573 grams of Desmodur™ N100 (available from Lanxess, Canada), 430 grams of poly(ethylene glycol) acrylate (Mn ~ 375, available from Sigma-Aldrich, Canada), 500 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA) and 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a –N=C=O peak at 2274 cm^{-1}. Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the –N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 8

[0098] A mixture of reactive iodonium tetraphenylborate having possible structures as in Figures 6, 7, 11, 12 and 13 was obtained by heating 320 grams of 1,3-dioxolane solution containing 573 grams of Desmodur™ N100 (available from Bayer Canada), 50 grams of 2-hydroxyethylmethacrylate (available from Sigma-Aldrich, Canada), 275 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 780 grams of dipentaerythritol pentaacrylate (SR-399 available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a –N=C=O peak at 2274 cm^{-1}. Then, 150 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum indicated that the –N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 9

[0099] A mixture of reactive iodonium tetraphenylborate having possible structures as in Figures 7, 9, 10, 11 and 12 was obtained by heating 137 grams of 1,3-dioxolane solution containing 245 grams of Desmodur™ N100 (available from Bayer Canada), 310 grams of poly(ethylene glycol) acrylate (Mn ~ 375, available from Sigma-Aldrich, Canada), 244 grams of pentaerythritol triacrylate (SR-444, available from Sartomer, USA), 100 grams of dipentaerythritol pentaacrylate (SR-399 available from Sartomer, USA), 1 gram of hydroquinone (available from Sigma-Aldrich, Canada) and 1 gram of dibutyl tin dilaurate (available from Sigma-Aldrich, Canada) to 60°C under an oxygen atmosphere and constant stirring for 10 hours. A sample of reaction mixture was withdraw from the reaction flask and its FTIR spectrum, recorded on KBr pellet, showed a –N=C=O peak at 2274 cm^{-1}. Then, 75 grams of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyliodonium tetraphenylborate (available from American Dye Source Inc., Canada) was slowly added into the reaction mixture, which was stirred at 60°C for an additional 6 hours. The FTIR spectrum then indicated that the –N=C=O peak at 2274 cm^{-1} had disappeared, which was indicative of the completion of the reaction. The clear viscous product obtained was ready for use.

EXAMPLE 10

[00100] Reactive iodonium salt having the structure as shown in Figure 14 was synthesized by slowly adding 31.5 grams of 2-isocyanato-ethylmethacrylate into 300 ml solution of 1,3-dioxolane dissolving with 80 grams of [2-[9,9-(3-hydroxypropyl)fluorenyl] 4-methylphenyliodonium triphenyl-n-butylborate and 0.1 grams of dibutyl tin dilaurate at 60°C under constant stirring and an oxygen atmosphere. The reaction was monitored by FTIR, which indicated that the reaction was completed within 5 hours. The product was precipitated in de-ionized water, filtered and washed copiously with de-ionized water. It was then washed with ether and dried in air until constant weight.

[00101] The iodonium salts of Figures 20-25 were also synthesized.

<u>Synthesis of Thermally Reactive Polymer Binders:</u>

EXAMPLE 11

[00102] The thermally reactive polymer binder, RPB-01 was synthesized by adding, by portions, 25 grams of hydroxypropyl cellulose (Klucel® E, available from Hercules, USA) to a reaction flask containing 500 grams of 1,3-dioxolane at 60°C, under air atmosphere and with constant stirring. After complete dissolution, 3 drops of dibutyl tin dilaurate, which acts as a catalyst for this reaction, were added to the flask. Then, 5.0 grams of 2-isocyanatoethylmethacrylate (available from American Dye Source, Canada) were slowly added to the reaction flask and the mixture was stirred at 60°C for 7 hours. FTIR spectrum of the polymer on KBr pellet indicated that the reaction was completed with the disappearance of the –N=C=O peak at 2274 cm^{-1}.

The ideal structure of RPB-01 is shown in Figure 15. n-Propanol was added into the reaction to provide 5.0 % solid content solution.

EXAMPLE 12

[00103] The reactive polymer binder, RPB-02 was synthesized in way similar to that of Example 11 with the exception that 10 grams of 2-isocyanatoethylmethacrylate was used in the reaction. The ideal structure of RPB-02 is similar to that of RPB-01 with more reactive functional groups present in the polymer. n-Propanol was added into the reaction to provide 5.0 % solid content solution.

EXAMPLE 13

[00104] The reactive polymer binder RPB-03 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 12.2 grams of 4-hydroxybenzaldehyde (100 mmole, available from Sigma-Aldrich, Canada) were slowly added to the flask and the mixture was stirred at 60°C for 4 hours. Then, 0.5 gram of sodium hydride (60 % in mineral oil, available from Sigma-Aldrich, Canada) was slowly added into the reaction. After hydrogen gas was no longer produced from the reaction, 3.0 grams of 3-bromopropyl-methacryloyl-ethyl carbamate was added into the reaction mixture. The reaction was continued for 5 hours at 60°C. The product was precipitated in de-ionized water, filtered and washed copiously with de-ionized water. It was then dried in air until constant weight. The ideal structure of RPB-03 is shown in Figure 16, wherein a= 9.00%, b=1.00%, d=88.00% and e=2.00%.

EXAMPLE 14

[00105] The reactive polymer binder RPB-04 was synthesized by adding, by portions, 90 grams of polyvinyl alcohol (Celvol™ 103, a 98% hydrolyzed polyvinyl acetate having an average molecular weight of about 18,000) to a reaction flask containing 500 grams of dimethylsulfoxide (DMSO) at 60°C, under nitrogen atmosphere and with constant stirring. After complete dissolution, 3 ml of concentrated sulfuric acid, which acts as a catalyst for this reaction, were added to the flask. After thirty minutes, 6.5 grams of butyraldehyde and 2.35 grams of acryloylpropyloxybenzaldehyde (available from American Dye Source Inc., Canada) were added into the reaction mixture. The reaction was continued for 5 hours at 60°C. The product was precipitated in de-ionized water, filtered and washed copiously with de-ionized water. It was then dried in air until constant weight. The ideal structure of RPB-04 is shown in Figure 17, wherein a= 9.00%, b=1.00%, d=88.00% and e=2.00%.

EXAMPLE 15

[00106] The reactive polymer binder, RPB-05 was synthesized by heating a mixture of 200 grams of anhydrous 1,3-dioxolane, dissolving with 15.0 g poly(ethylene glycol) acrylate (Mn ~ 2,010, available from American Dye Source Inc., Canada), 15.0 g styrene, 50.0 g acrylonitrile and in a 1L 4-neck flask at 75°C under a nitrogen atmosphere and constant stirring. After heating for 30 minutes, 0.5 g of Vazo™ 64 was added to the reaction mixture. After 10 hours of polymerization at 75°C, another 0.5 g of Vazo™ 64 was added into the reaction mixture and the polymerization was continued for another 14 hours. Air was introduced into the reaction mixture and it stirring at 75°C continued for an additional 2 hours to terminate the polymerization. The reaction temperature was lowered to 5°C and 4 grams of triethylamine were added into the reaction mixture. Then, a solution containing 10 grams of 1,3-dioxolane and 2 grams of acryloyl chloride was slowly introduced into the reaction. The reaction was stirred at room temperature for 5 hours. The product was precipitated in water and dried until constant weight. The molecular weight of RPB-03 was determined to be around 28,000 with a polymer dispersity of 1.4. The ideal structure of RPB-05 is shown in Figure 18, wherein a=86.16 %, b=13.16 % and c=0.68 %.

[00107] An emulsion of RPB-05 was prepared by slowly adding 50 grams of de-ionized water into 200 grams n-propanol solution, in which 80 grams of RPB-03 were dissolved, using a high shear mixer set at 7,500 rpm.

EXAMPLE 16

[00108] The reactive polymer binder, RPB-06 was synthesized by heating a mixture of 200 grams of n-propanol and 50 grams of de-ionized water, which in which 15.0 g poly(ethylene glycol) acrylate (Mn ~ 2,000, available from American Dye Source Inc., Canada) were dissolved, 5.0 grams of N-methoxymethylmethacrylamide (available from American Dye Source Inc., Canada), 15.0 g styrene and 50.0 g acrylonitrile, in a 1L 4-neck flask at 75°C under a nitrogen atmosphere and constant stirring. After heating for 30 minutes, 0.5 g of Vazo™ 64 was added into the reaction mixture. The solution became hazy within 30 minutes of polymerization. After polymerization for 10 hours at 75°C, another 0.5 g of Vazo™ 64 was added into the reaction mixture and the polymerization was continued for another 14 hours. Air was introduced into the reaction mixture and stirring at 75°C was continued for an additional 2 hours to terminate the polymerization. The molecular weight of RPB-06 was determined to be around 29,000 with polymer dispersity of 1.7. The ideal structure of RPB-06 is shown in Figure 19, wherein a=82.88 %, b=12.66 %, c= 3.81 % and d=0.65 %.

On-Press Developable Negative-Working Lithographic Printing Plates

EXAMPLE 17

[00109] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m^2.

Composition	**From example**	**% by Solid Weight**
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	0.50
RPB-05	14	2.15
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00110] The plate was imaged between 100 and 250 mJ/cm^2 and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies.

EXAMPLE 18

[00111] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m^2.

Composition	**From example**	**% by Solid Weight**
PVA-02	2	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	0.50
RPB-05	14	2.15
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00112] The plate was imaged between 100 and 250 mJ/cm^2 and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies

EXAMPLE 19

[00113] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m^2.

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	0.50
RPB-06	15	2.15
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00114] The plate was imaged between 100 and 250 mJ/cm^2 and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies

EXAMPLE 20

[00115] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m^2.

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	1.00
RPB-03	15	1.65
3-Mercapto triazol		0.25

Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00116] The plate was imaged between 100 and 250 mJ/cm^2 and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies

EXAMPLE 21

[00117] A coating solution with the following composition was coated on a brush-grained, phosphoric acid anodized aluminum substrate using wire-wound rod and dried at 80°C with hot air. The obtained coating weight was around 1.0 g/m^2.

Composition	From example	% by Solid Weight
PVA-01	1	2.00
Iodonium Salt Mixture	9	5.00
RPB-01	10	1.00
RPB-04	15	1.65
3-Mercapto triazol		0.25
Blue Color Former (*)		0.10
n-Propanol		90.0
Water		10.0
BYK 336		0.10
(*) Blue Color Former is Blue-63 (available from Yamamoto Chemicals Inc., Japan)		

[00118] The plate was imaged between 100 and 250 mJ/cm^2 and mounted on the AB Dick press. High quality printing image was obtained on paper after 10 impressions. The plate can be used to print more than 20,000 high-resolution copies

[00119] Although the present invention has been described hereinabove by way of specific embodiments thereof, it can be modified, without departing from the spirit and nature of the subject invention as defined in the appended claims.

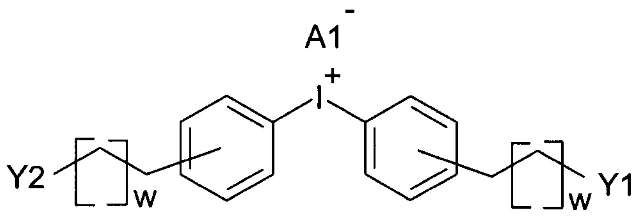
WHAT IS CLAIMED IS:

1. An iodonium salt having attached thereto at least one first functional group capable of undergoing cationic or radical polymerization.

2. The iodonium salt of Claim 1 wherein said first functional group is acrylate, methacrylate or vinyl ether.

3. The iodonium salt of Claim 1 or 2 wherein said first functional group is attached to an aryl ring of the iodonium salt via an urethane or an urea bond.

4. The iodonium salt of any one of Claims 1 to 3 having as a general formula:



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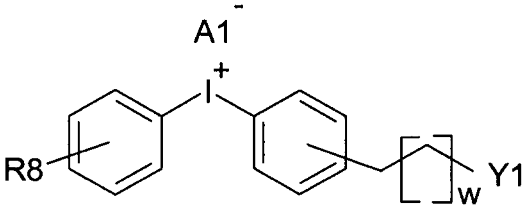

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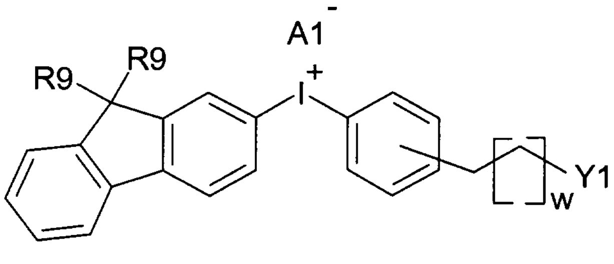

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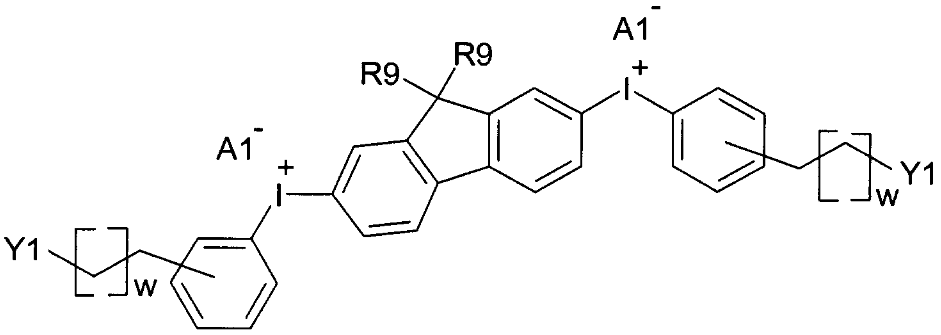


wherein:

- A1 is a tosylate, triflate, hexafluoroantimonate, tetrafluoroborate, tetraphenylborate or triphenyl-n-alkylborate anionic counter ion;
- w may vary between 0 and 18;
- R8 and R9 are independently hydrogen, linear $C_1 - C_{18}$ alkyl, branched $C_1 - C_{18}$ alkyl, alkyl oxy, poly(ethylene oxide) or poly(propylene oxide); and
- Y1 and Y2 each independently represent an urethane-containing substituent having attached thereto said first functional group.

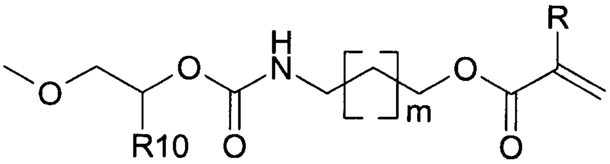
5. The iodonium salt of Claim 4 wherein at least one of R8 or R9 has attached thereto said first functional group.

6. The iodonium salt of Claims 4 or 5 wherein at least one of Y1 or Y2 has been produced by reacting a mono-isocyanate, a di-isocyanate or a poly-isocyanate with an amine or an alcohol having attached thereto said first functional group.

7. The iodonium salt of Claim 6 wherein said mono-isocyanate, di-isocyanate or poly-isocyanate is Desmodur N100, Desmodur N3300, Desmodur CB 75N, Desmodur I, Desmodur W, Desmodur M, Desmodur H or Desmodur TD80.

8. The iodonium salt of Claim 6 or 7 wherein said alcohol is pentaerylthritol triacrylate, dipentaerylthritol pentaacrylate, 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylacrylate, 4-hydroxybutylmethacrylate, 6-hydroxyhexylacrylate, 6-hydroxyhexylmethacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate or poly(propylene glycol) acrylate and poly(propylene glycol) methacrylate.

9. The iodonium salt of Claim 4 or 5 wherein at least one of Y1 or Y2 is:



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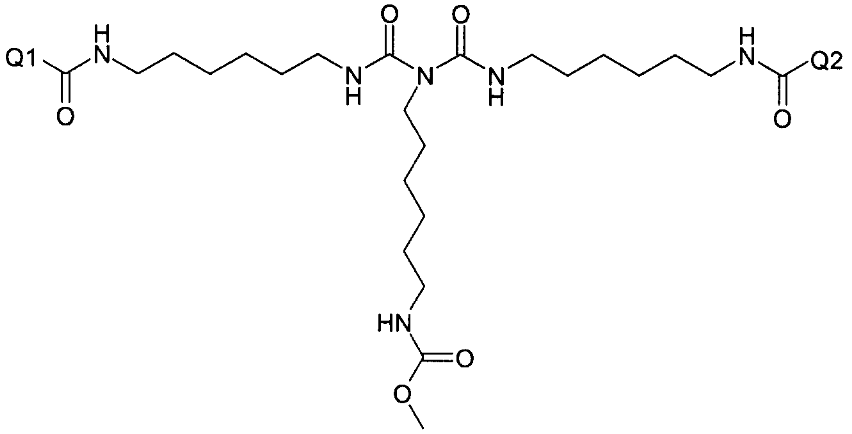

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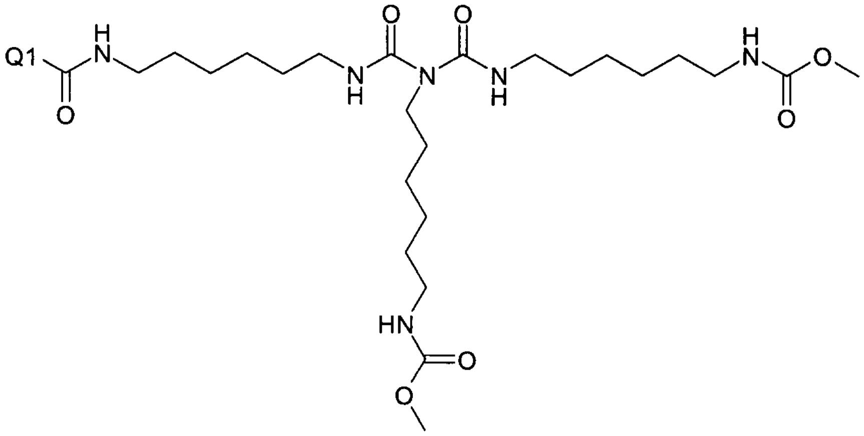
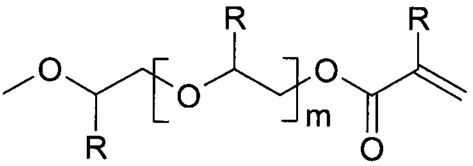


wherein:

- R is hydrogen or methyl,
- m varies between 1 and 18,
- R10 is hydrogen, linear or branched C1-C18 alkyl chain; and
- Q1 and Q2 each independently represent an end compound having attached thereto said first functional group.

10. The iodonium salt of Claim 9 wherein at least one of Q1 or Q2 is :



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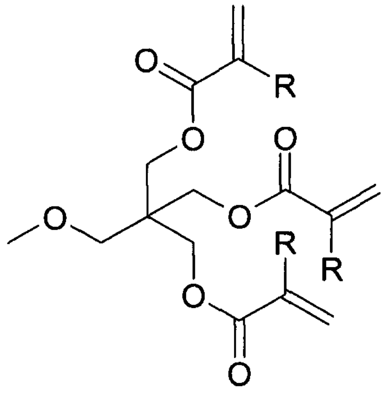

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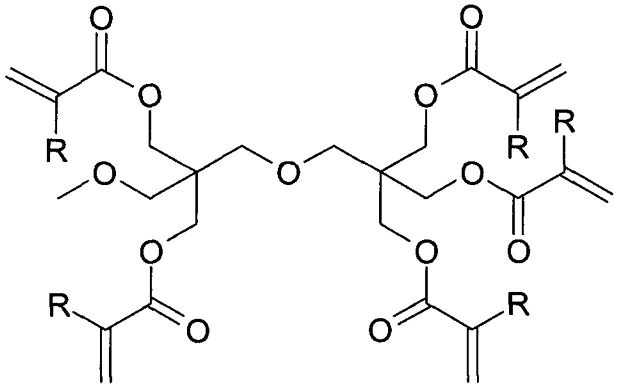
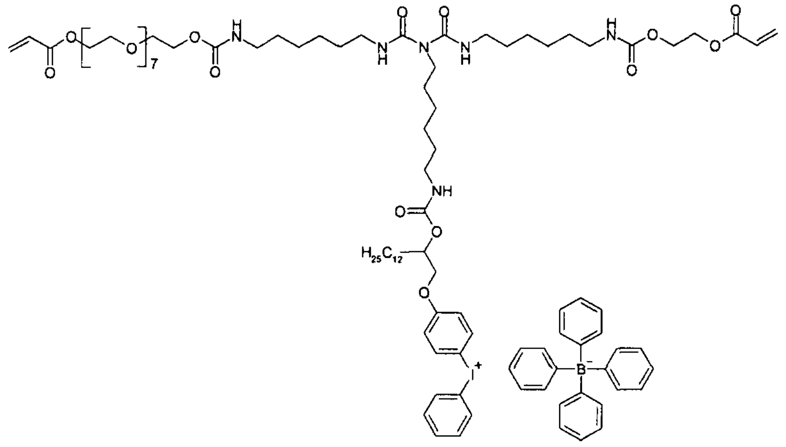


wherein R is hydrogen or methyl.

11. The iodonium salt of Claim 10 being:



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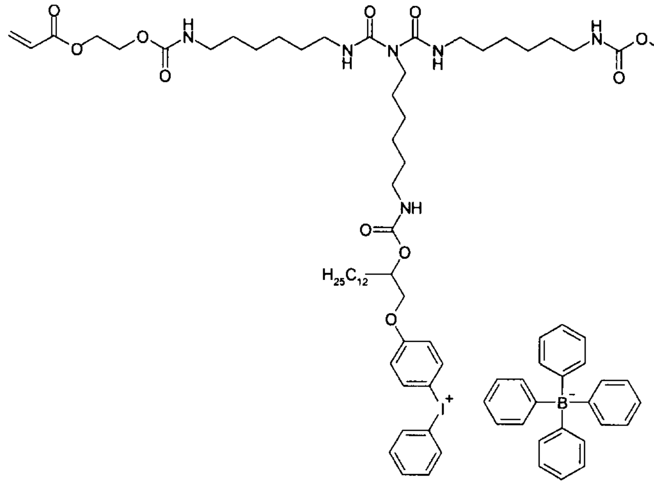

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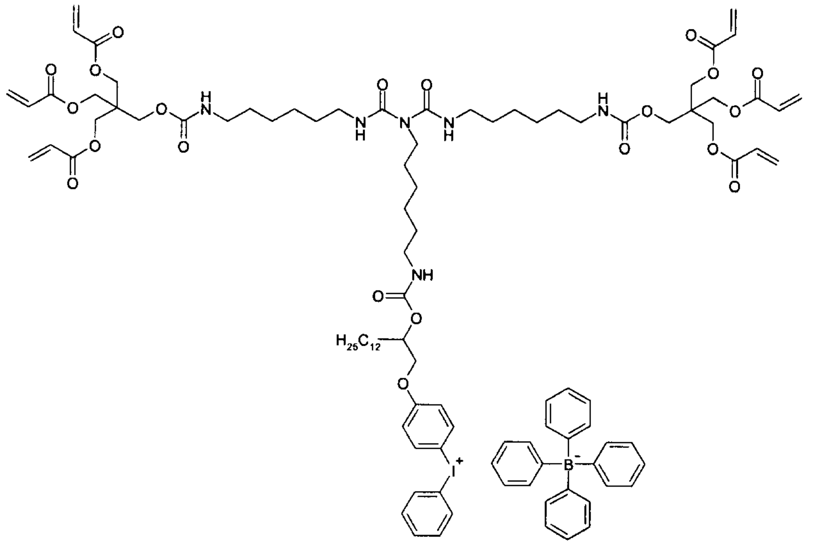

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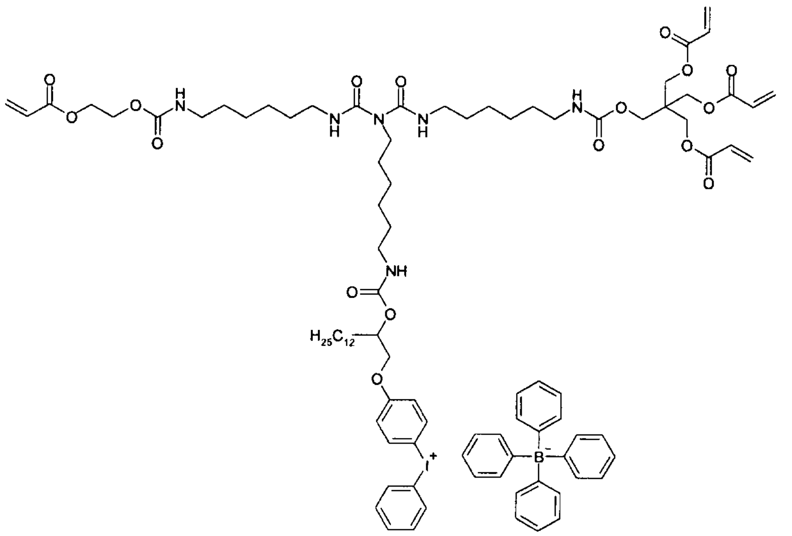

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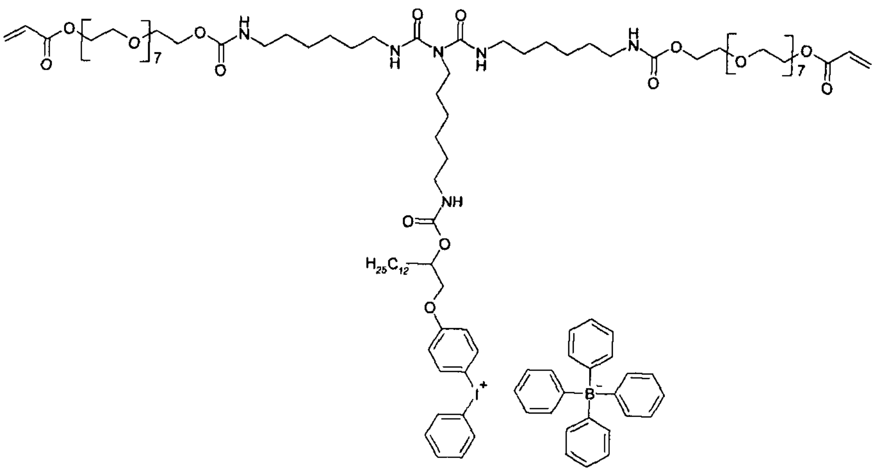
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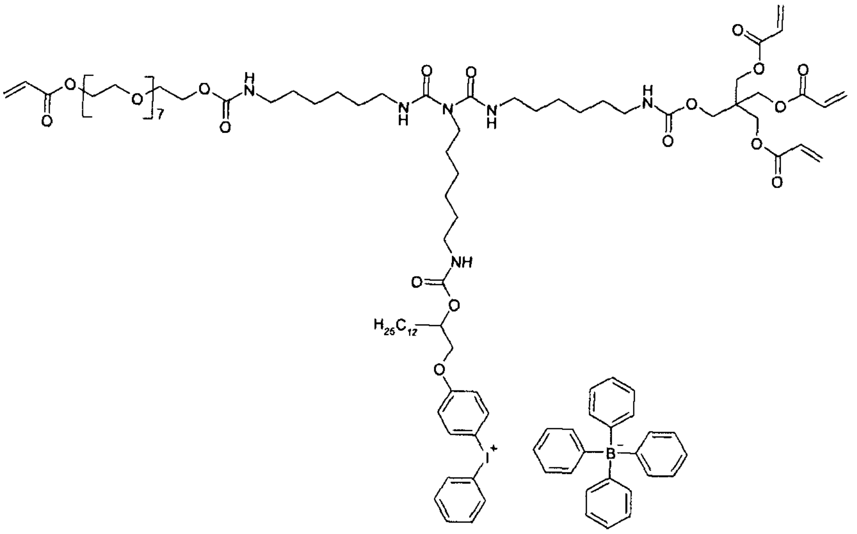
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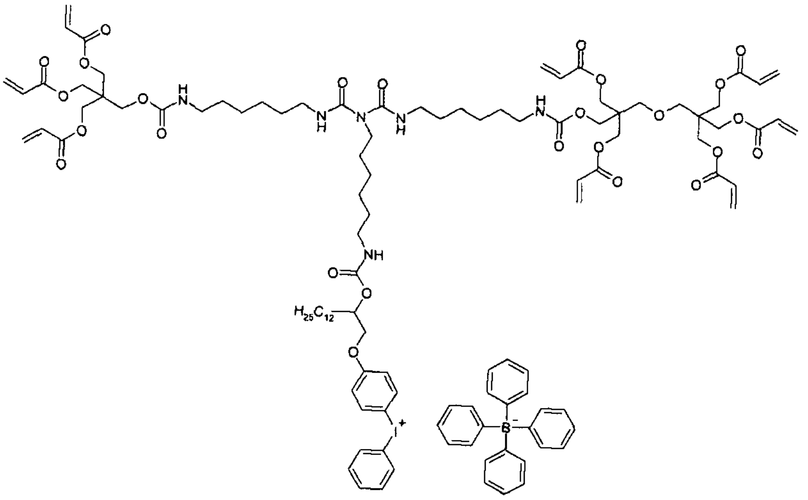
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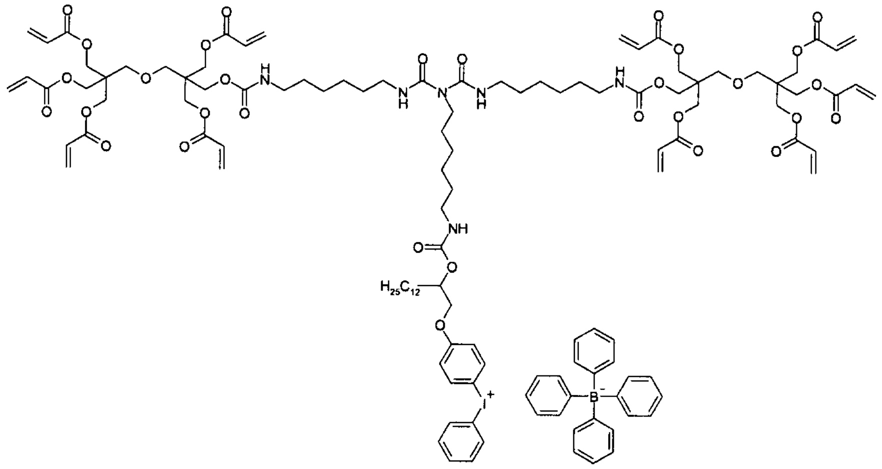

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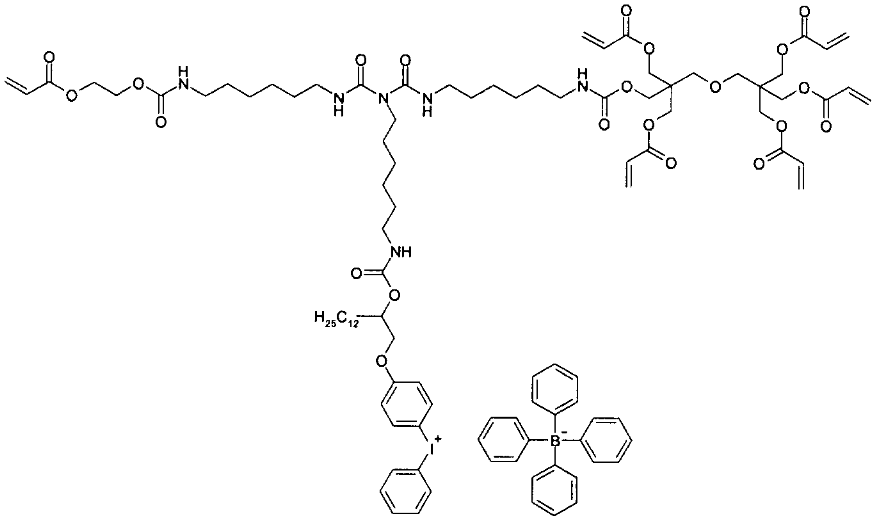

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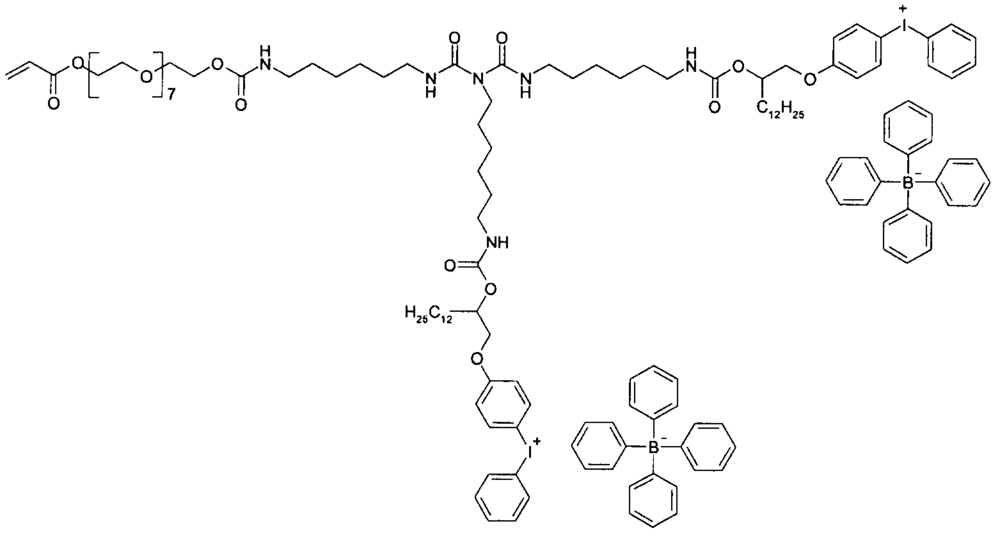

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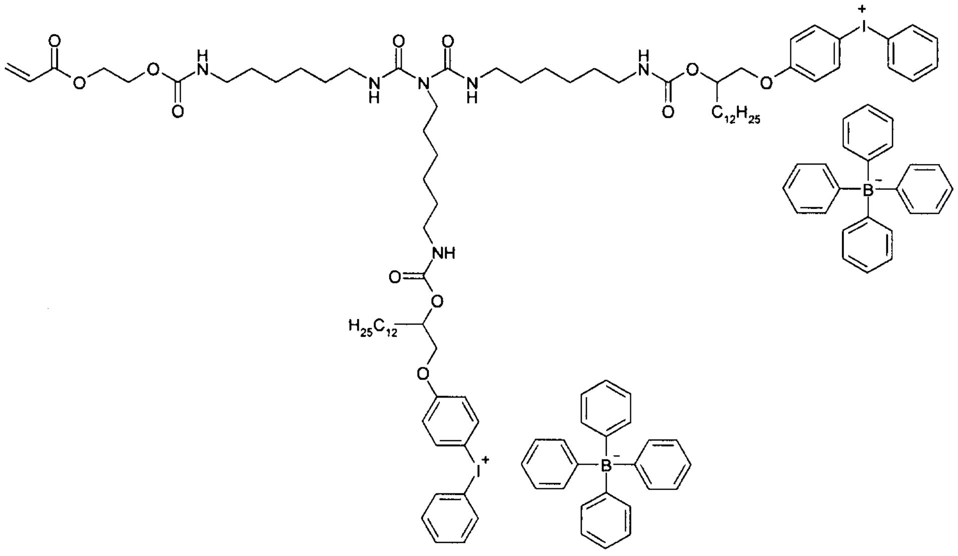

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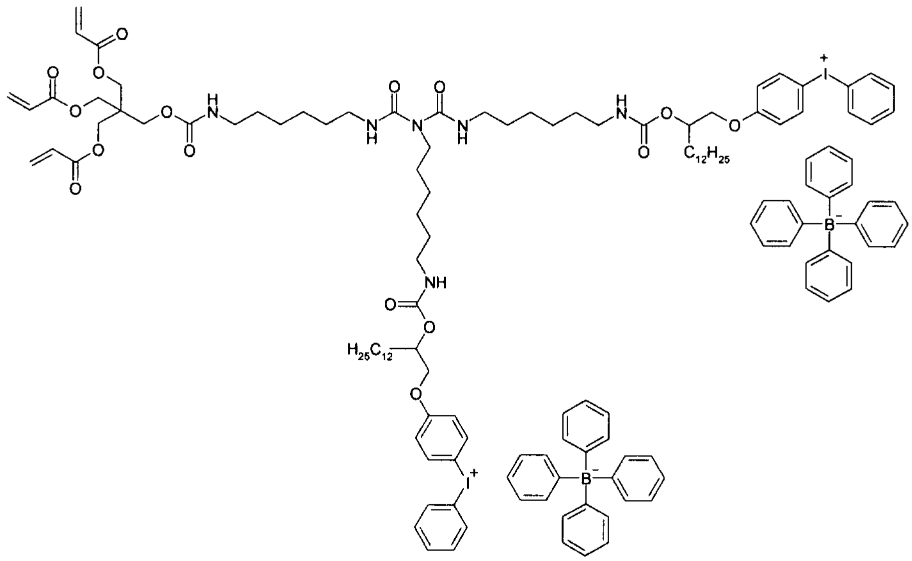

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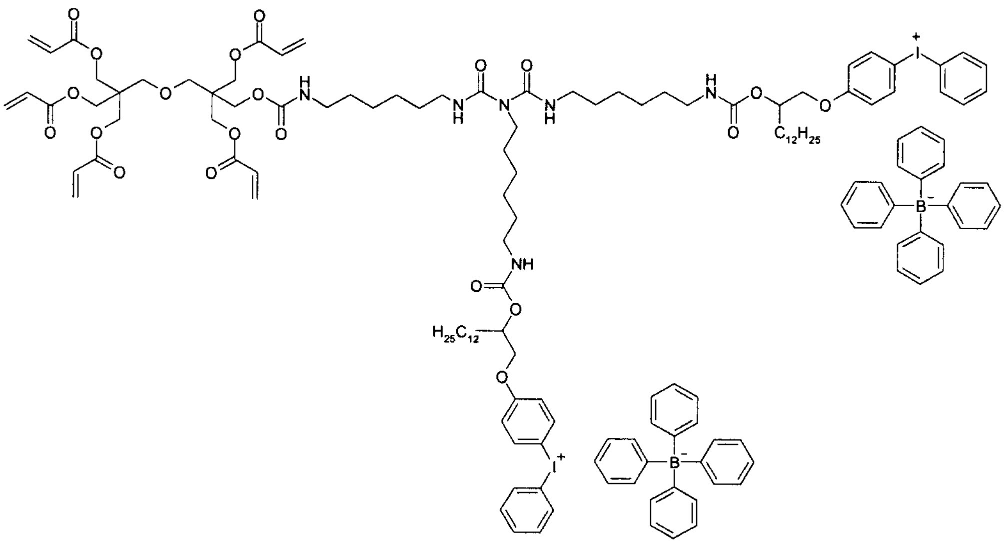

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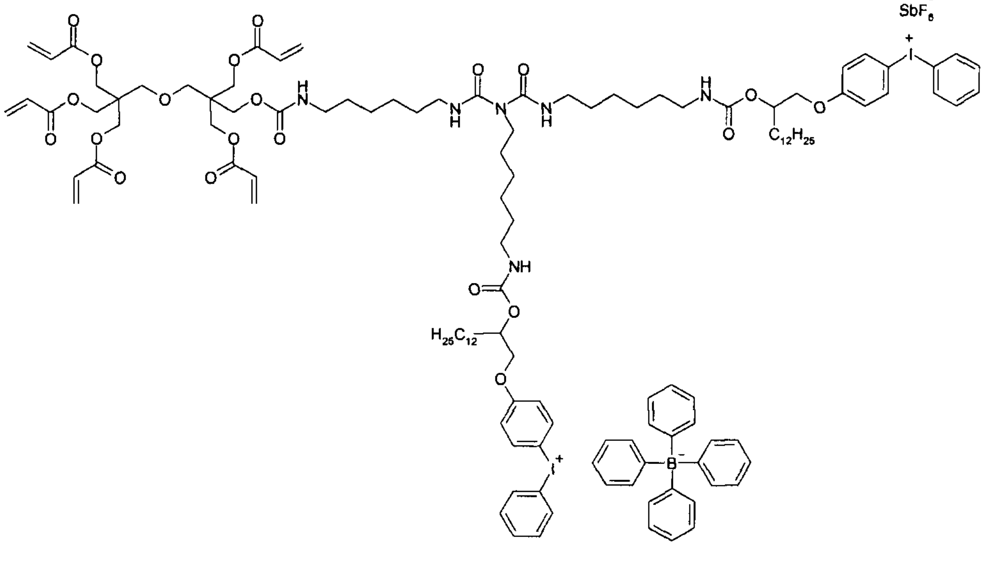

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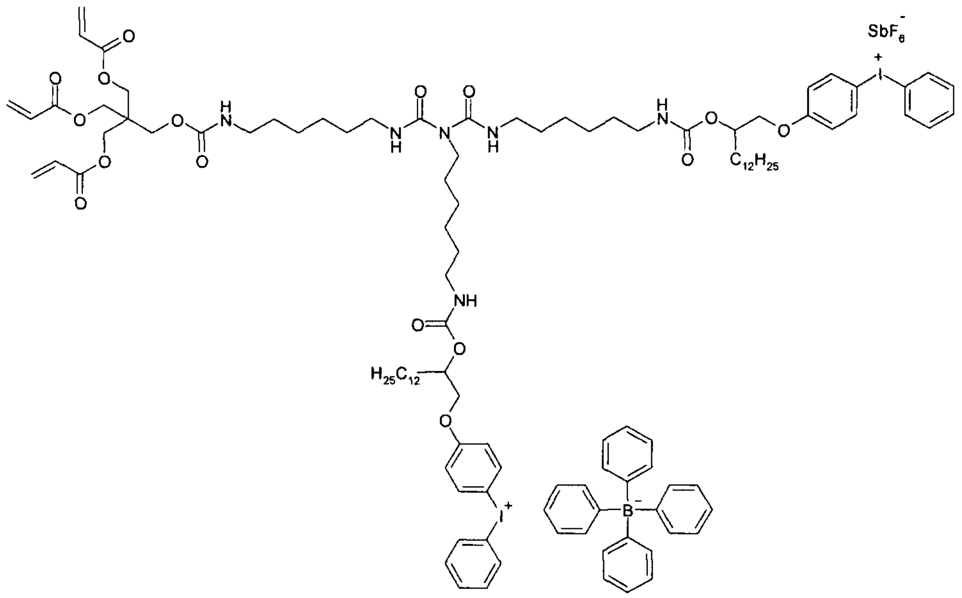

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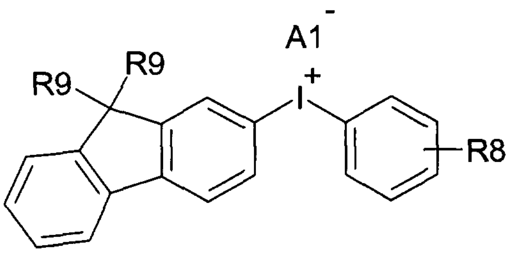
12. The iodonium salt of any one of Claims 1 to 3 having the general structure:



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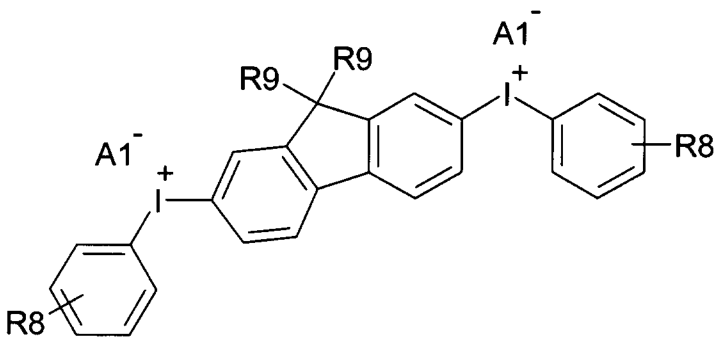
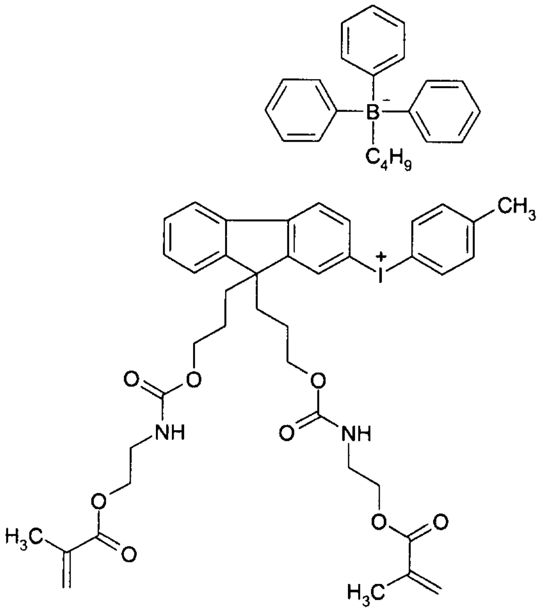


wherein:

- A1 represents a tosylate, triflate, hexafluoroantimonate, tetrafluoroborate, tetraphenylborate and triphenyl-n-alkylborate anionic counter ion; and
- R8 and R9 are independently hydrogen, linear $C_1 - C_{18}$ alkyl, branched $C_1 - C_{18}$ alkyl, alkyl oxy, poly(ethylene oxide) or poly(propylene oxide),

and wherein at least one of R8 or R9 is not hydrogen and has attached thereto said first functional group.

13. The iodonium salt of Claim 12 being:



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14. A method of preparing the iodonium salts of any one of Claims 2 to 13 comprising attaching a pendant group to an iodonium salt, wherein said

pendant group is obtained by reacting a mono-isocyanate, a di-isocyanate or a poly-isocyanate with an amine or an alcohol, wherein said amine or alcohol are terminated by an acrylate, a methacrylate or a vinyl-ether.

15. The method of claim 14 wherein the mono-isocyanate, di-isocyanate or poly-isocyanate is Desmodur™ N100, Desmodur™ N3300, Desmodur™ CB 75N, Desmodur™ I, Desmodur™ W, Desmodur™ M, Desmodur™ H or Desmodur™ TD 80.

16. The method of claim 14 or 15, wherein the alcohol is pentaerylthritol triacrylate, 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 4-hydroxybutylacrylate, 4-hydroxybutylmethacrylate, 6-hydroxyhexylacrylate, 6-hydroxyhexylmethacrylate, poly(ethylene glycol) acrylate, poly(ethylene glycol) methacrylate, poly(propylene glycol) acrylate or poly(propylene glycol) methacrylate.

17. Use of the iodonium salt of any one of Claims 1 to 13 or a mixture thereof in the preparation of a coating.

18. The use of Claim 17 wherein the coating is a negative working lithographic printing plate coating.

19. A lithographic printing plate coating solution comprising the iodonium salt of any one of Claims 1 to 13 or a mixture thereof.

20. The coating solution of Claim 19 comprising from about 5% to about 60 % by solid weight of said iodonium salt.

21. The coating solution of Claim 19 or 20 further comprising a near infrared absorbing dye.

22. The coating solution of Claim 21 wherein said near infrared absorbing dye is a molecular dye, a dimeric dye, a dendrimeric dye or a polymeric dye.

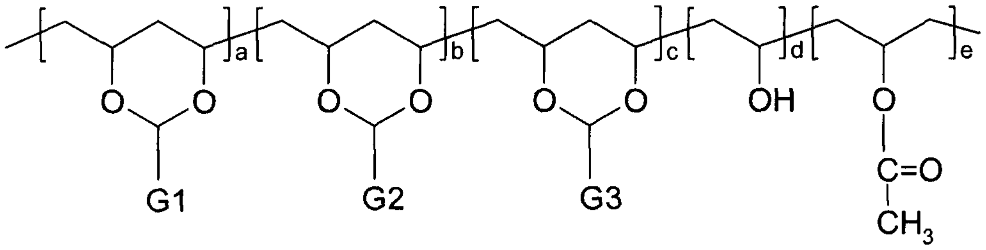
23. The coating solution of Claim 21 or 22 wherein said near infrared absorbing dye is a first acetal copolymer or a mixture thereof.

24. The coating solution of Claim 23 comprising from about 5% to about 50 % by solid weight of said first acetal copolymer.

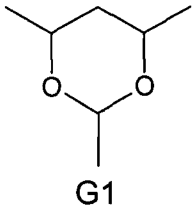
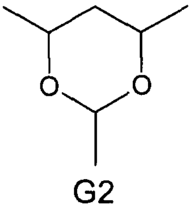
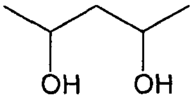
25. The coating solution of Claim 23 or 24 wherein said first acetal copolymer has attached thereto at least one second functional group capable of undergoing

cationic or radical polymerization.

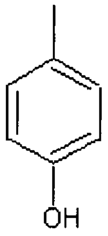
26. The coating solution of any one of Claims 23 to 25 wherein the first acetal copolymer has the following structure:



wherein:

- G1 represents a processing segment providing solubility in organic solvents;
- G2 represents a thermal reactive segment;
- G3 represents a radiation-absorbing segment exhibiting one or more strong absorption peaks between 700 and 1100 nm;
- a, b, c, d and e are molar ratios and may vary from 0.01 to 0.99;
- any of  and  may independently be replaced by , and
- said second functional group, if present, is attached to G2 or G3.

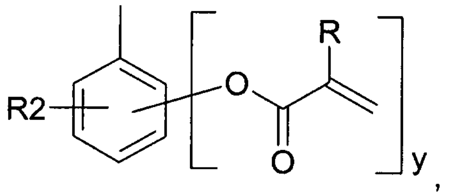
27. The coating solution of Claim 26 wherein G1 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, said linear aryl or branched aryl comprise a cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide methylbenzylsufonyl-carbamat, carboxylic acid or phosphoric acid functional group.

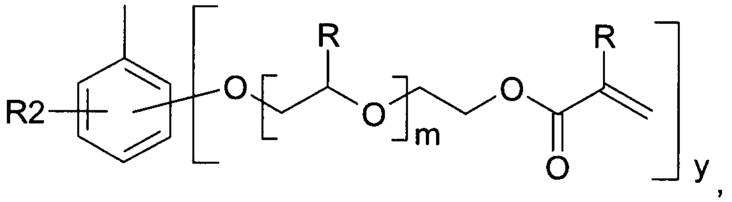
28. The coating solution of Claim 27 wherein G1 is  .

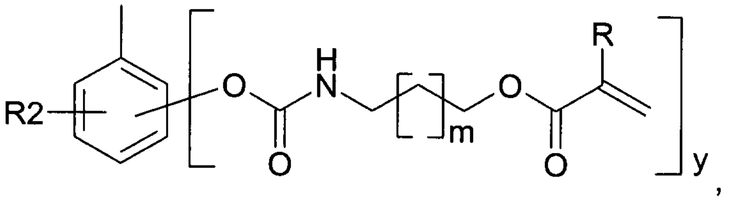
29. The coating solution of any one of Claims 26 to 28 wherein G2 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl has attached thereto said second functional group.

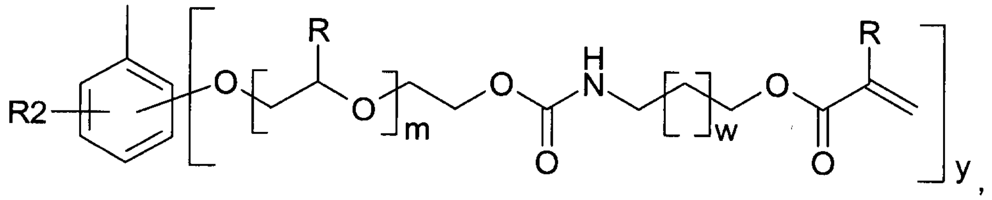
30. The coating solution of Claim 29 wherein said second functional group is vinyl ether, alkoxy-methyl acrylamide, alkoxy methacrylamide, acrylate or methacrylate.

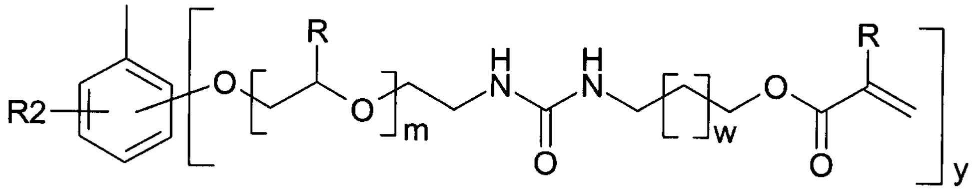
31. The coating solution of Claim 30 wherein G2 is:



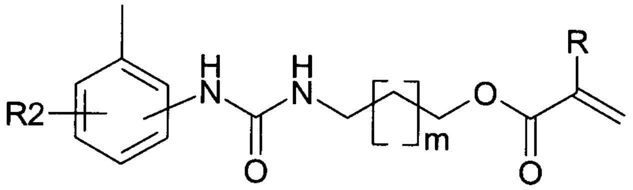








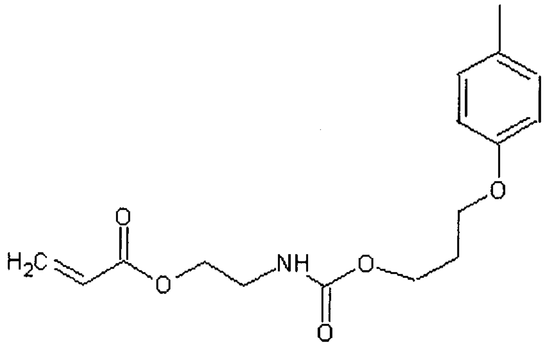
or



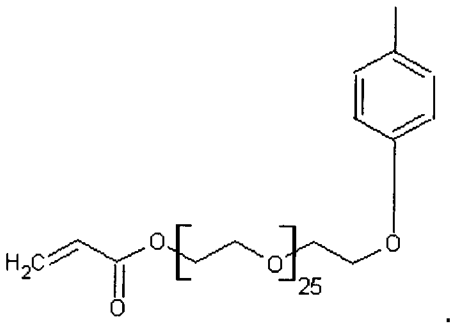
wherein:

- R is hydrogen or methyl;
- R2 is C1 – C8 alkyl or alkoxy;
- m and w may vary between 0 and 50; and
- y is 1 or 2.

32. The coating solution of Claim 30 where G2 is:



or



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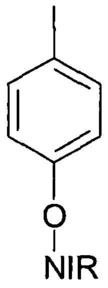
33. The coating solution of any one of Claims 26 to 32 wherein said first acetal copolymer comprises more than one G3 segments that may identical to or different from each other.

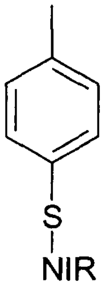
34. The coating solution of any one of Claims 26 to 33 wherein G3 further exhibits

one or more strong absorption peaks between 400 and 700 nm.

35. The coating solution of any one of Claims 26 to 34 wherein G3 is:



or



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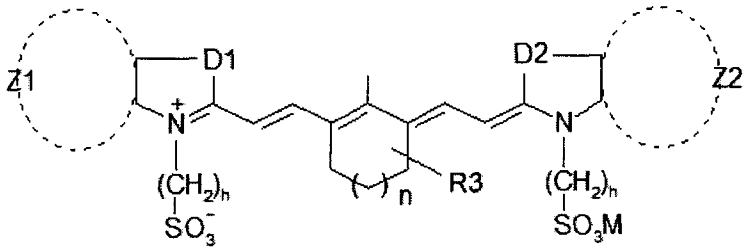
wherein NIR is a near-infrared absorbing chromophore exhibiting one or more strong absorption peaks between 700 and 1100 nm.

36. The coating solution of Claim 35 wherein said near-infrared absorbing chromophore is:



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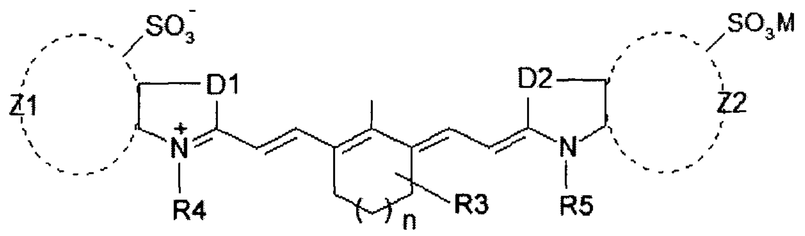

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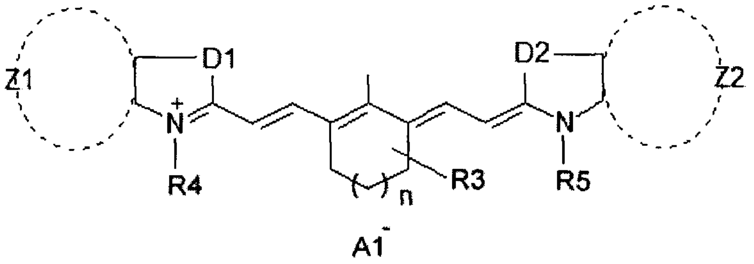

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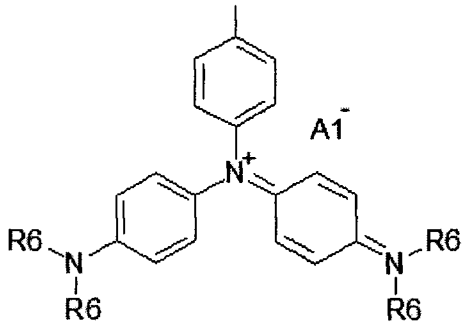
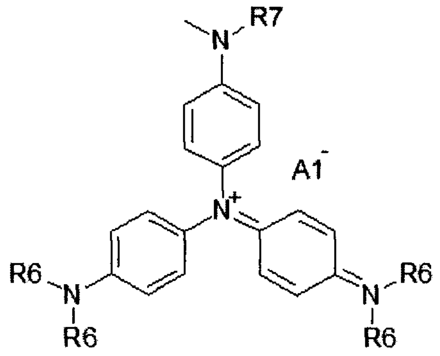


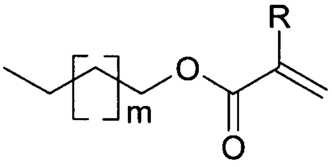
, or



wherein:

- D1 and D2 are –O-, -S-, -Se-, -CH = CH-, or -C(CH3)2;
- Z1 and Z2 each independently represent one or more fused substituted or unsubstituted aromatic ring;
- h may vary from 2 to 8;
- n represents 0 or 1;
- M represents hydrogen or Na, K, or tetraalkylammonium salts cationic counter ion.
- A1 represents bromide, chloride, iodide, tosylate, triflate, trifluoromethane carbonate, dodecyl benzosylfonate or tetrafluoroborate, tetraphenylborate and triphenyl-n-butylborate anionic counter ion.
- R3 and R7 each independently represent hydrogen or alkyl;
- R4, R5 and R6 each independently represent alkyl, aryl alkyl, hydroxy alkyl, amino alkyl, carboxy alkyl, sulfo alkyl or a polymerizable

substituent, said substituent comprising said second functional group and being of formula:



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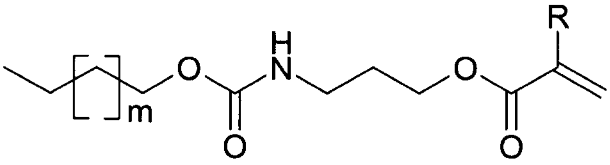

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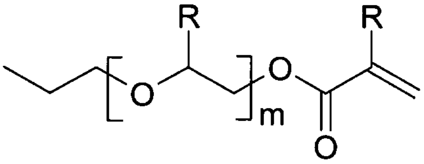

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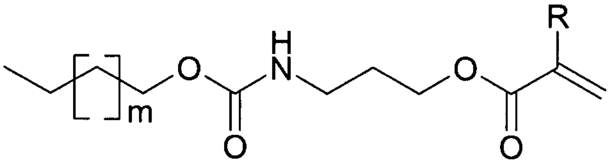
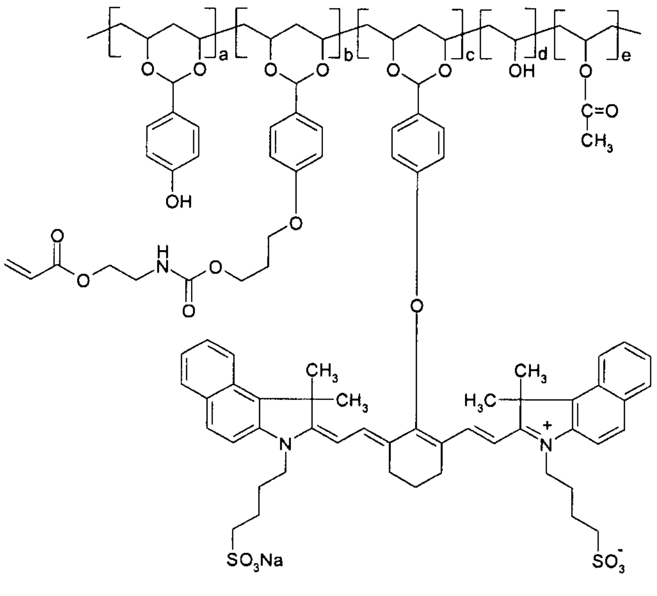


wherein m may vary between 0 and 50 and R is hydrogen or methyl.

37. The coating solution of Claim 36 wherein at least one of Z1 or Z2 is phenyl or naphtyl.

38. The coating solution of Claim 26 wherein said first acetal polymer is:



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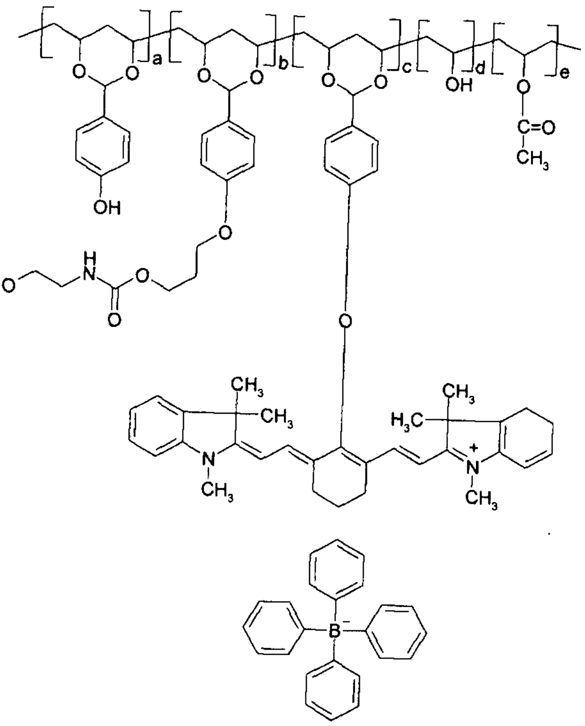

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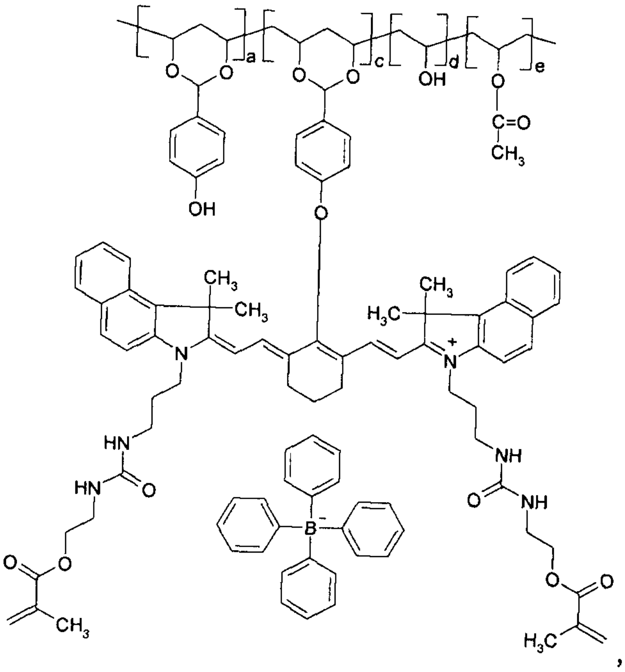
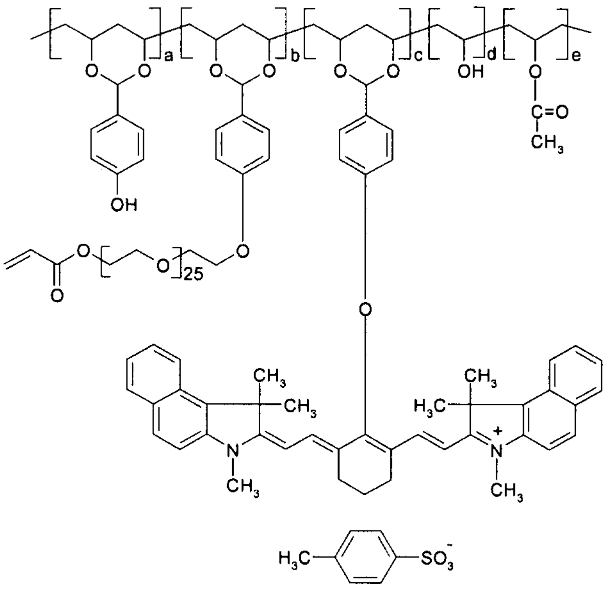


, or



wherein a, b, c, d and e are molar ratios that can vary from 0.01 to 0.99.

39. The coating solution of any one of claims 19 to 38 further comprising a polymer binder.

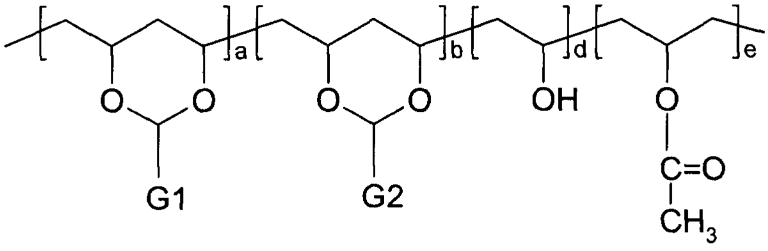
40. The coating solution of Claim 39 comprising from about 1% to about 50 % by solid weight of said polymer binder.

41. The coating solution of Claim 39 or 40 wherein said polymer binder has attached thereto at least one third functional group capable of undergoing cationic or radical polymerization.

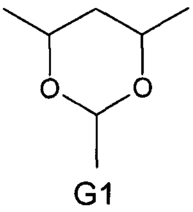
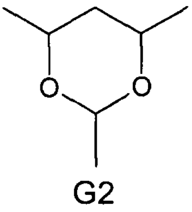
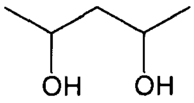
42. The coating solution of Claim 41 wherein said third functional group is acrylate, methacrylate, vinyl ether, hydroxyl, alkoxy-methyl acrylamide, alkoxy methacrylamide, N-methoxymethylacrylamide or N-methoxymethylmethacrylamide.

43. The coating solution of any one or Claims 39 to 42 wherein said polymer binder is a second acetal copolymer or a mixture thereof.

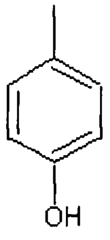
44. The coating solution of Claim 43 wherein said second acetal copolymer has the following structure:



wherein

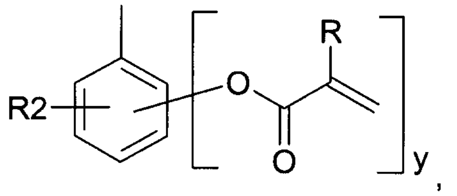
- G1 represents an processing segment providing solubility in organic solvents;
- G2 represents an thermal reactive segment;
- a, b, d and e are molar ratios and may vary from 0.01 to 0.99; and
- any of  and  may independently be replaced by 
- said third functional group, if present, is attached to G2.

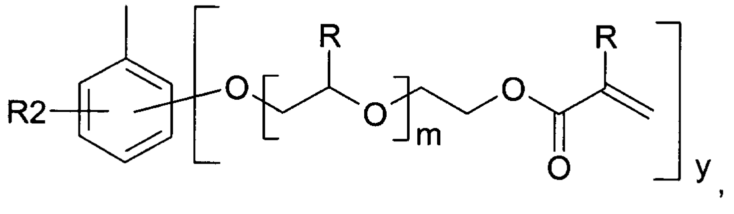
45. The coating solution of Claim 44 wherein G1 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl comprise a cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide methylbenzylsufonyl-carbamat, carboxylic acid or phosphoric acid functional group.

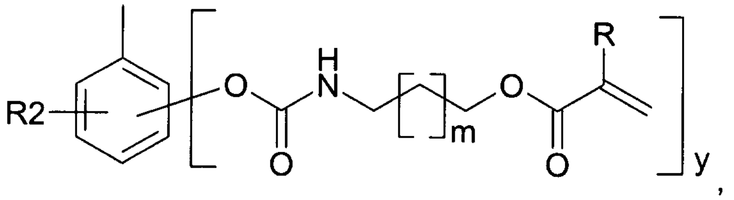
46. The coating solution of Claim 44 wherein G1 is C_3H_7 or  .

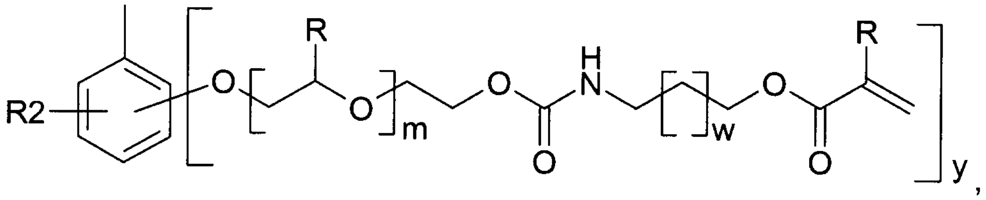
47. The coating solution of any one of Claims 44 to 46 wherein G2 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl has attached thereto said third functional group.

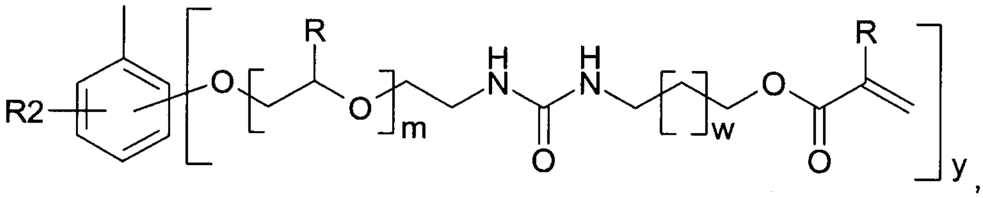
48. The coating solution of Claim 47 wherein G2 is:



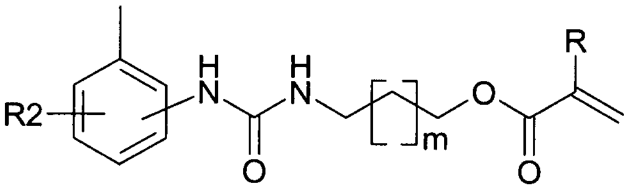








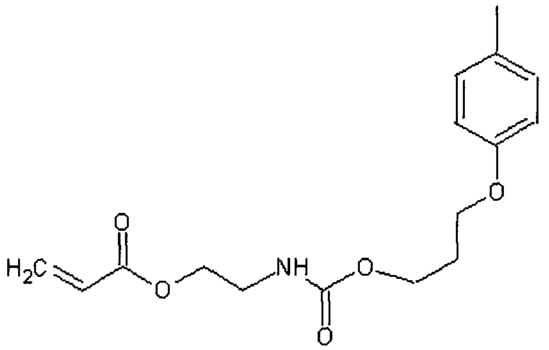
or



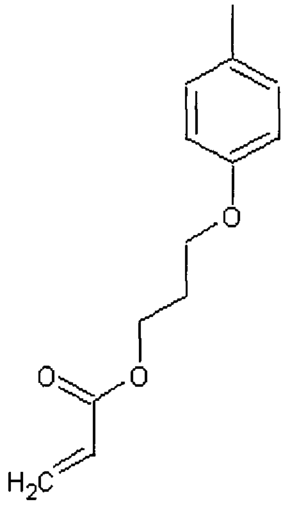
wherein:

- R is hydrogen or methyl;
- R2 is C1 – C8 alkyl or alkoxy;
- m and w may vary between 0 and 50; and
- y is 1 or 2.

49. The coating solution of Claim 47 wherein G2 is:



or



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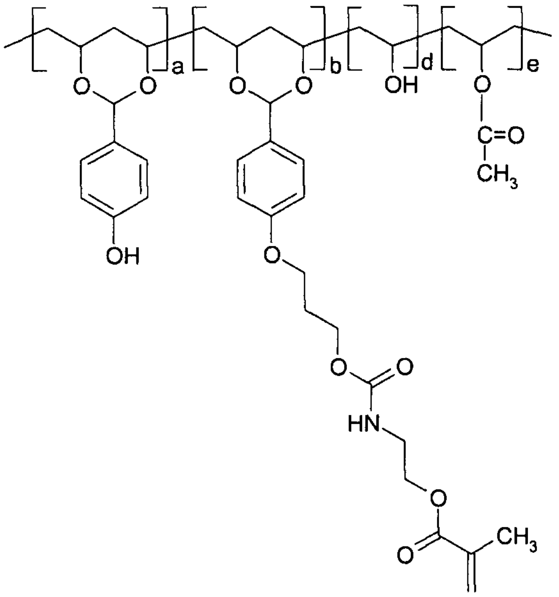
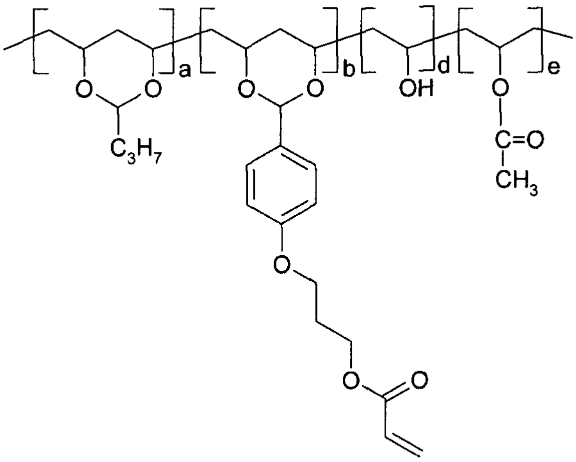
50. The coating solution of Claim 49 wherein said polymer binder is:



, or



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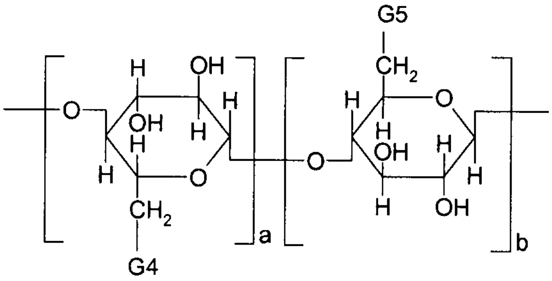
51. The coating solution of any one of Claims 41 or 42 wherein said polymer binder is selected from the group consisting of solvent-soluble cellulose ether

and water-soluble cellulose ether or a mixture thereof, said cellulose ethers having attached thereto said third functional group.

52. The coating solution of Claim 51 wherein said cellulose ethers have been modified by reacting a hydroxymethyl, a hydroxyethyl or a hydroxypropyl group attached to said cellulose with a 2-isocyanato-ethyl compound having attached thereto said third functional group.

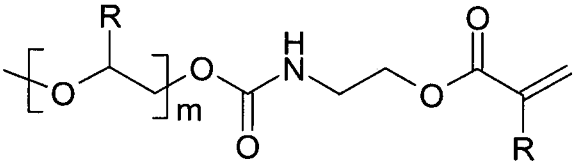
53. The coating solution of Claim 51 or 52 wherein said polymer binder has the following structure:



wherein:

- a and b are molar ratios and may vary between about 0.01 and about, 0.99,
- G4 is hydroxy, hydroxyethyl or hydroxypropyl; and
- G5 comprises said third functional group.

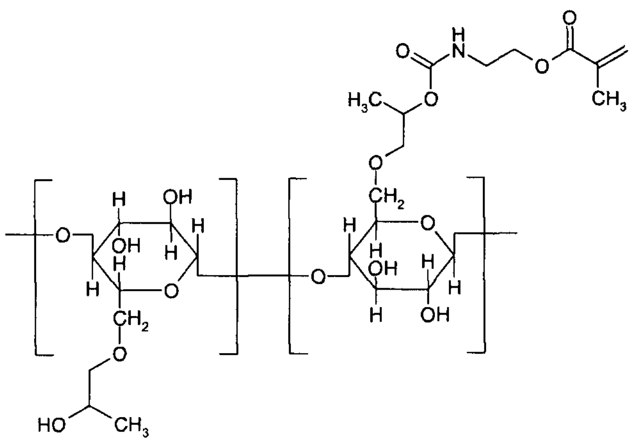
54. The coating solution of Claim 53 wherein G5 is



and

wherein m is 0 or 1 and R is hydrogen or methyl.

55. The coating solution of Claim 54 wherein said polymer binder has the following structure:



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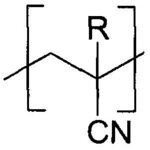
56. The coating solution of any one or Claims 41 or 42 wherein said polymer binder is a copolymer comprising one or more first monomers of formula:



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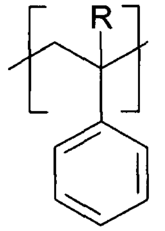

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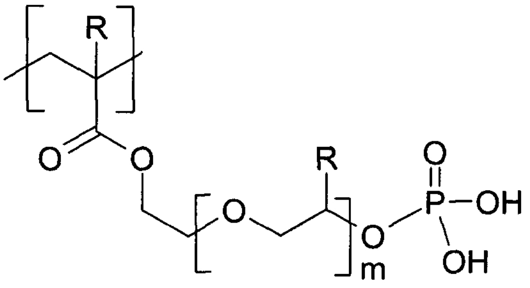

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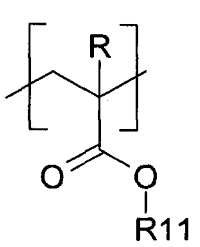

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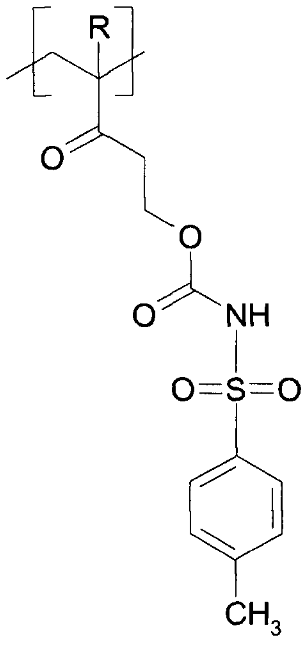

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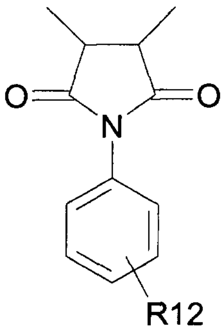

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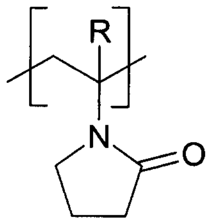

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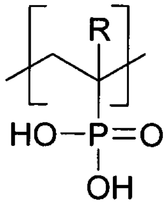
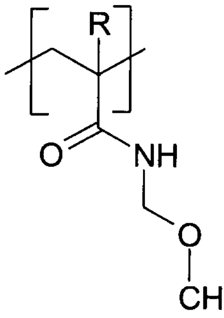


and one or more second monomers of general formula:



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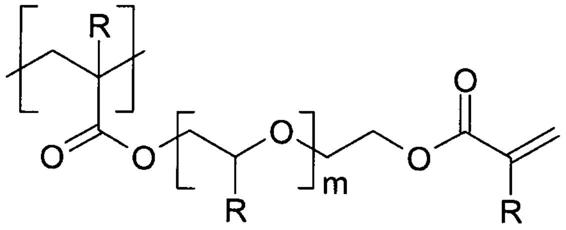

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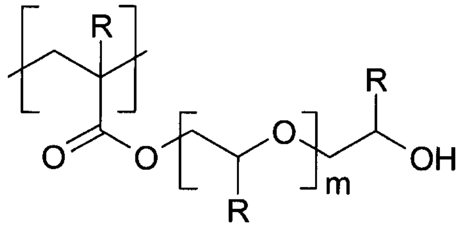

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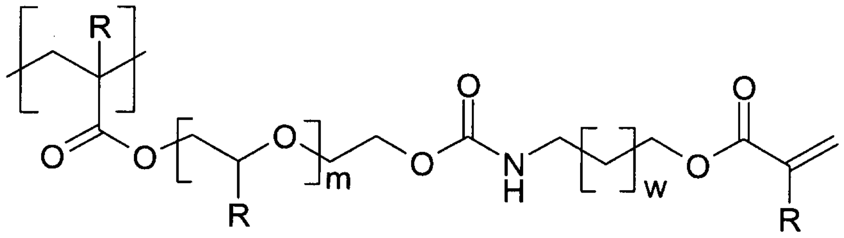

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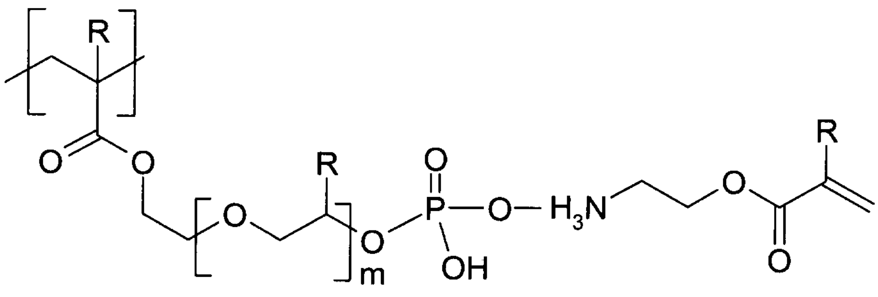
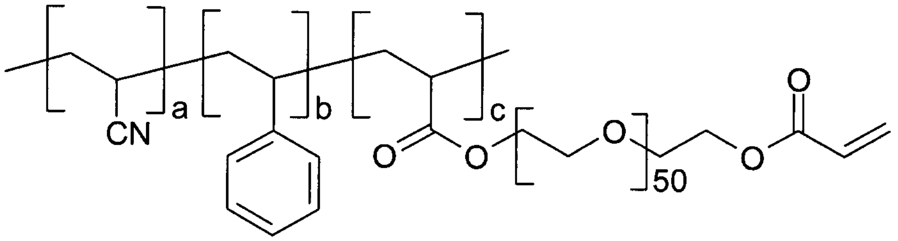


wherein:

- m and w may vary between 0 and 50;
- R is hydrogen or methyl;
- R11 is linear or branched alkyl chain; and

- R12 is alkyl, hydroxyl or carboxylic acid.

57. The coating solution of Claim 56 wherein said polymer binder is:



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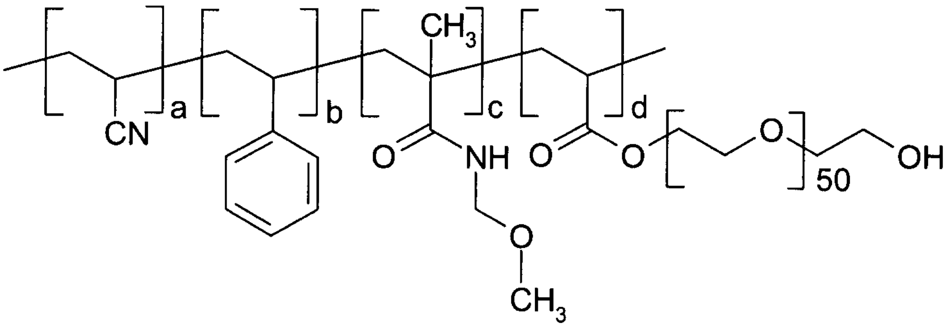


wherein a, b, c and d are molar ratios and may vary between about 0.01 and about 0.99.

58. The coating solution of any one of Claims 19 to 57 further comprising a colorant.

59. The coating solution of Claim 58 comprising from about 0.5% to about 5 % by solid weight of said colorant.

60. The coating solution of Claim 58 or 59 wherein said colorant is triarylpyridine, xanthene, isobenzofuranone, or lactone.

61. The coating solution of any one of Claims 58 to 60 wherein said colorant is initially colorless and becomes colored in the presence of free radical or acid.

62. The coating solution of any one of Claim 58 to 61 wherein said colorant is:

3',6'-bis[N-[2-chlorophenyl]-N-methylamino]spiro[2-butyl-1,1-dioxo[1,2-benz isothiazole-3(3H),9'-(9H)xanthene]];

3',6'-bis[N-[2-[methanesulfonyl]phenyl]-N-methylamino]spiro[2-butyl-1,1-dio xo[1,2-benzisothiazole-3(3H),9'-(9H)xanthene]];

9-Diethylamino[spiro[12H-benzo(a)xanthene-12,1'(3'H)-isobenzofuran)-3'-one];

2'-di(phenylmethyl)amino-6'-[diethylamino]spiro[isobenzofuran-1(3H),9'-(9H)-xanthen]-3-one ;

3-[butyl-2-methylindol-3-yl]-3-[1-octyl-2-methylindol-3-yl]-1-(3H)-isobenzo furanone;

6-[dimethylamino]-3,3-bis[4-dimethylamino]-phenyl-(3H)-isobenzofuranone;

2-[2-Octyloxyphenyl]4-[4-dimethylaminophenyl]-6-phenylpyridine; or

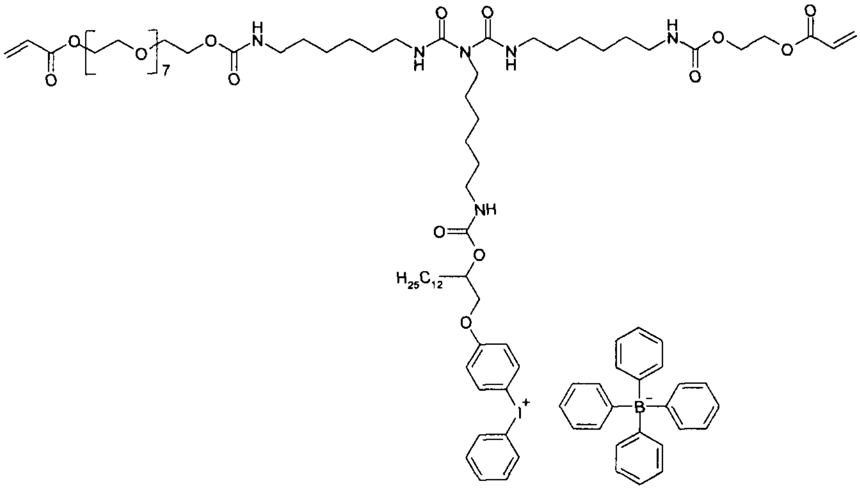
leuco lactone dyes, including Blue-63, GN-169 and Red-40.

63. The coating solution of any one of Claims 19 to 62 further comprising a stabilizer.

64. The coating solution of Claim 63 comprising from about 0.5% to about 5 % by solid weight of said stabilizer.

65. The coating solution of Claim 63 or 64 wherein said stabilizer is of methoxyphenol, hydroxyphenol, phenothiazine, 3-mercapto triazol or monomethyl ether hydroquinone.

66. The coating solution of Claim 19 comprising the iodonium salt of formula:



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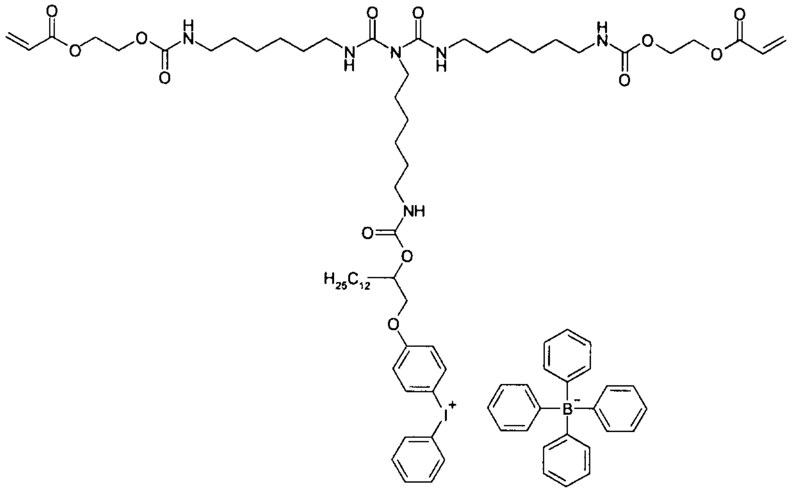

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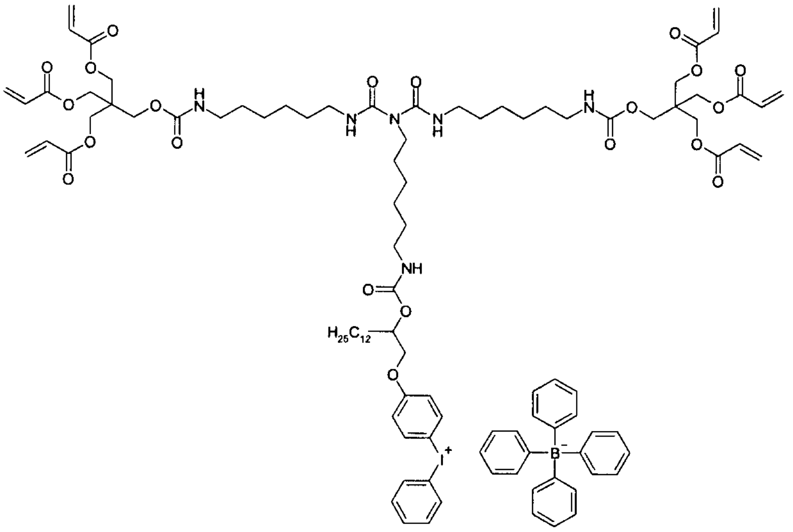

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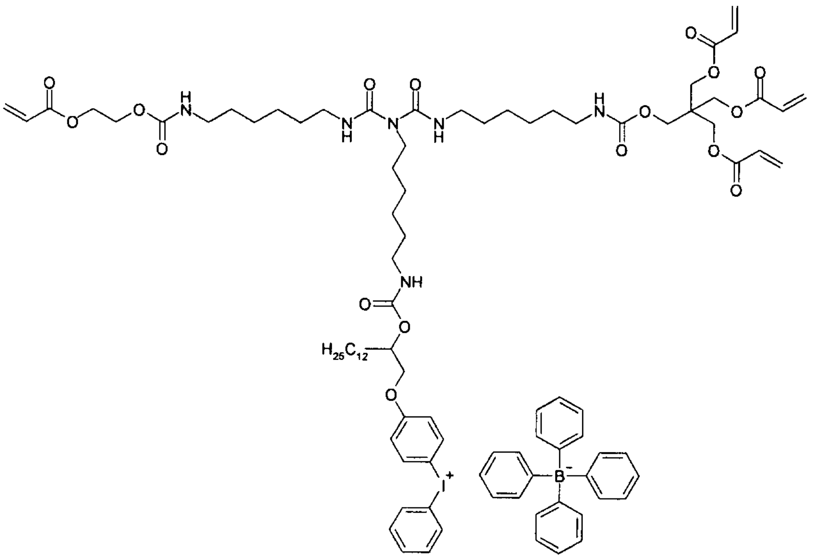

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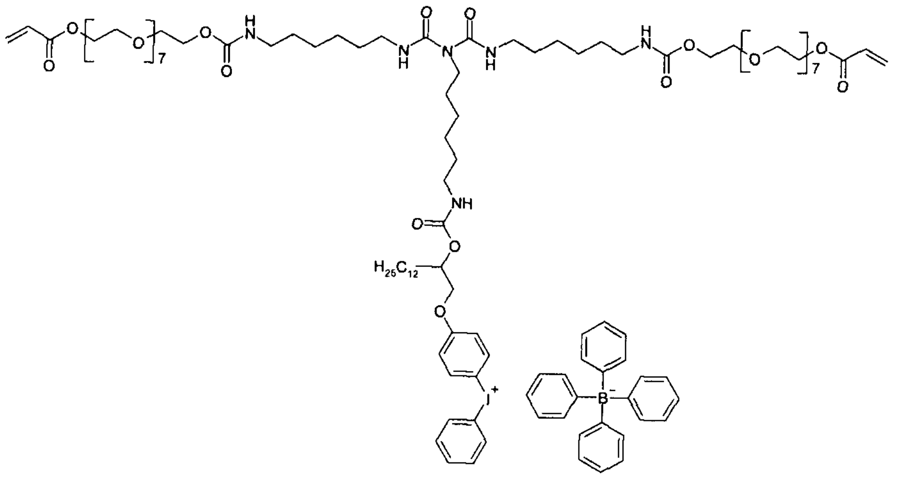

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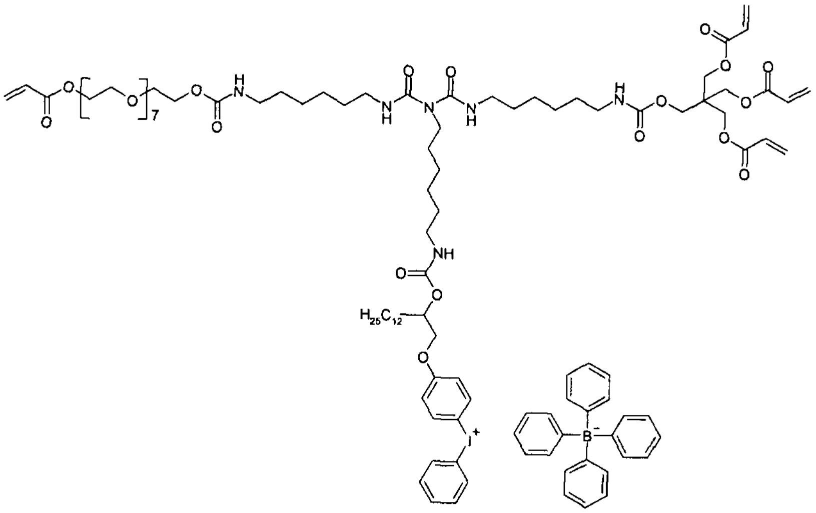

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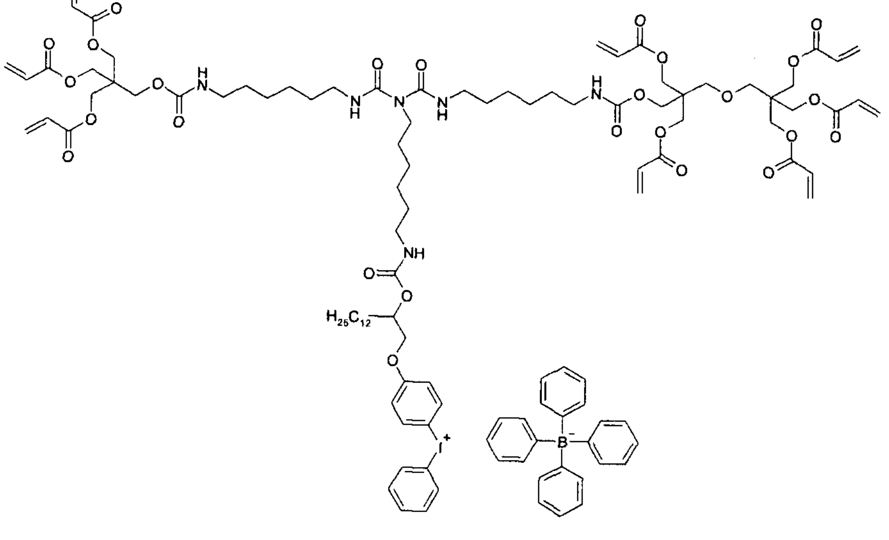

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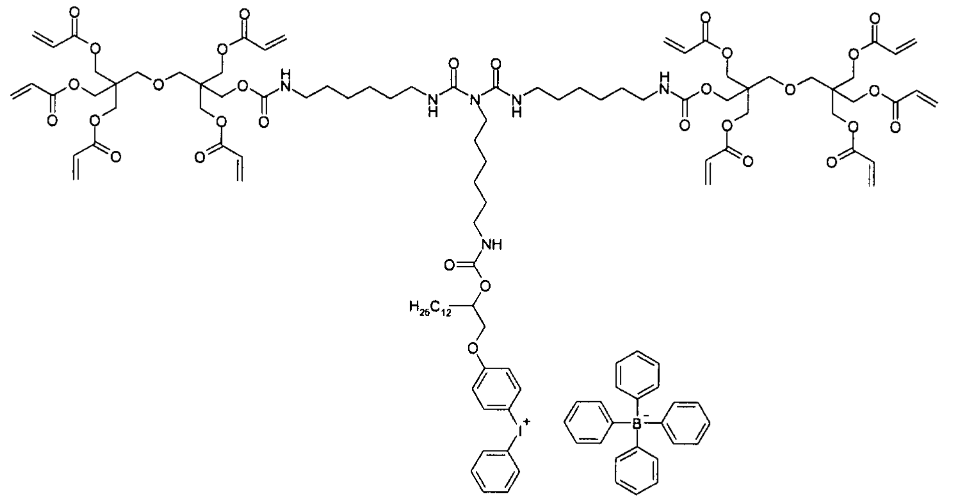

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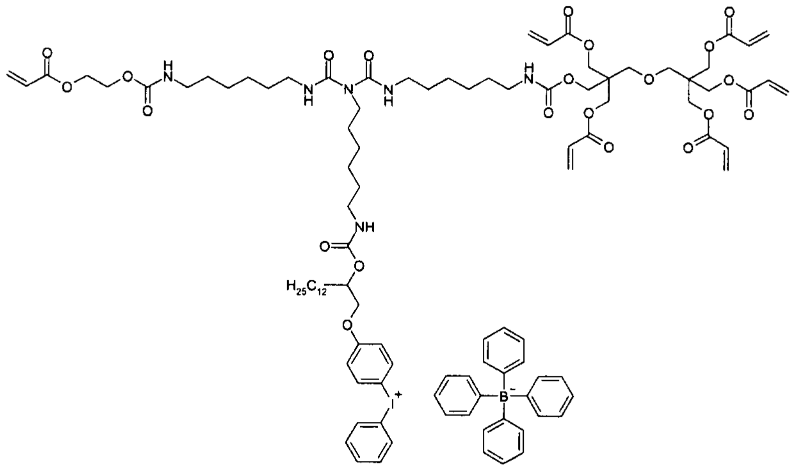

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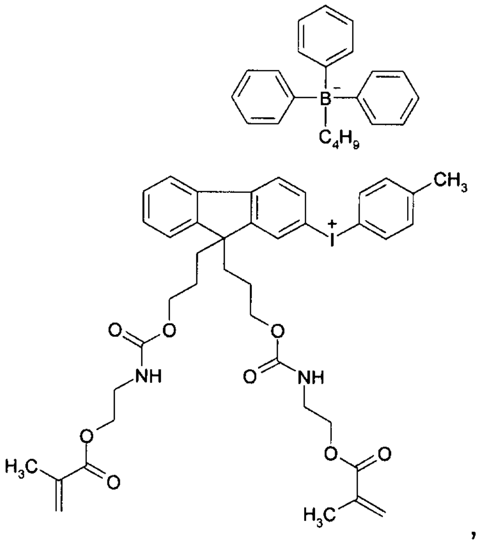

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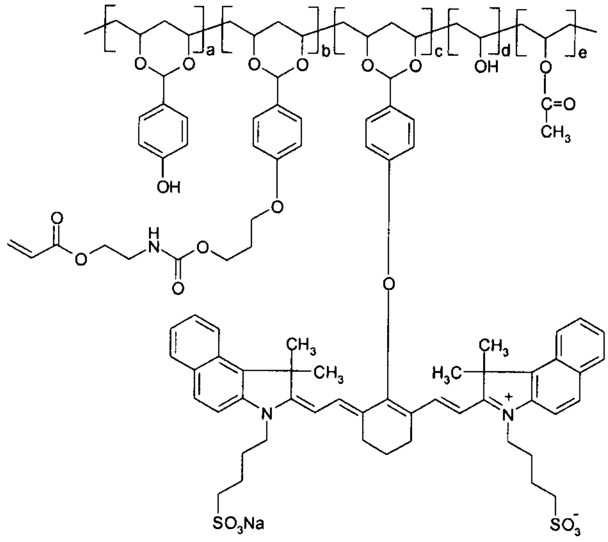
an acetal copolymer of formula:



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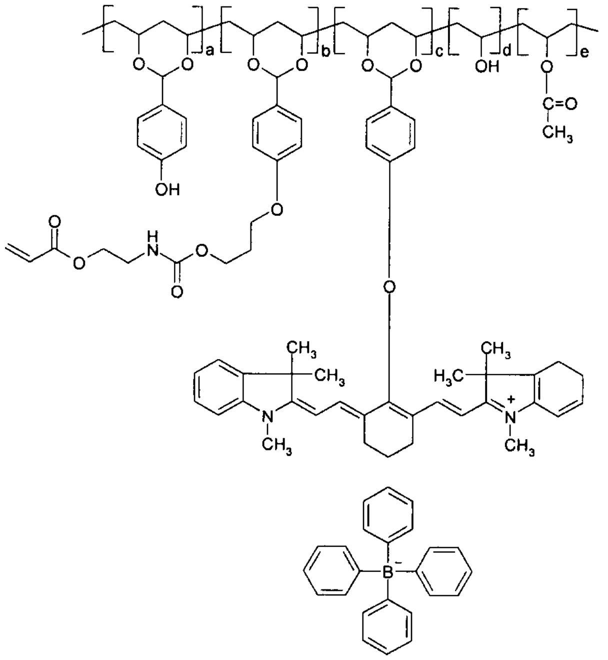

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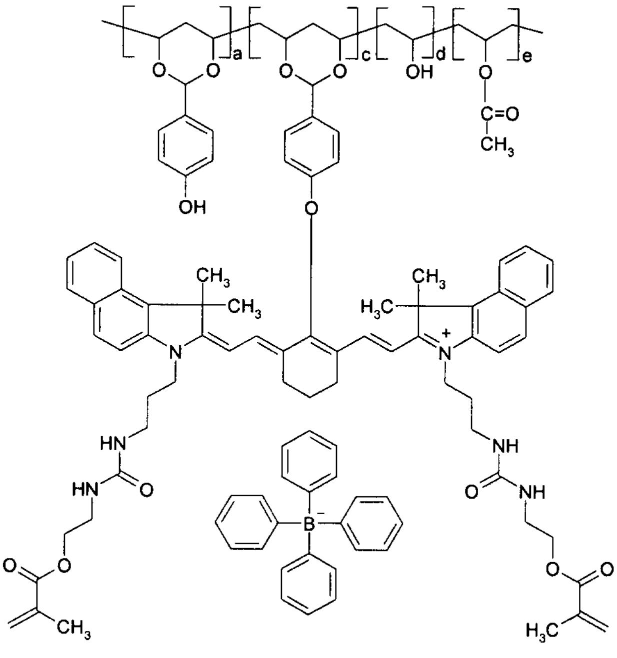

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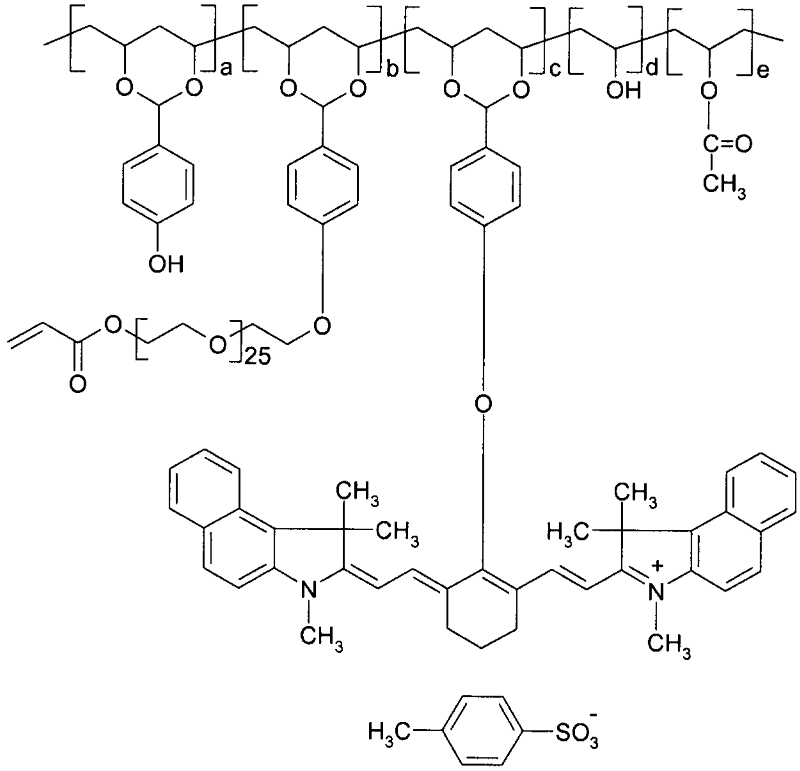
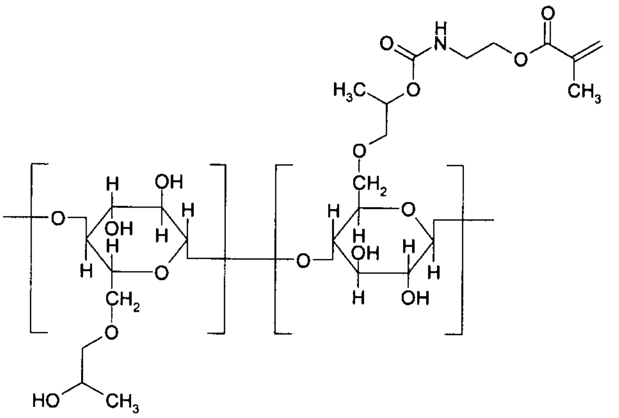


and a polymer binder of formula:



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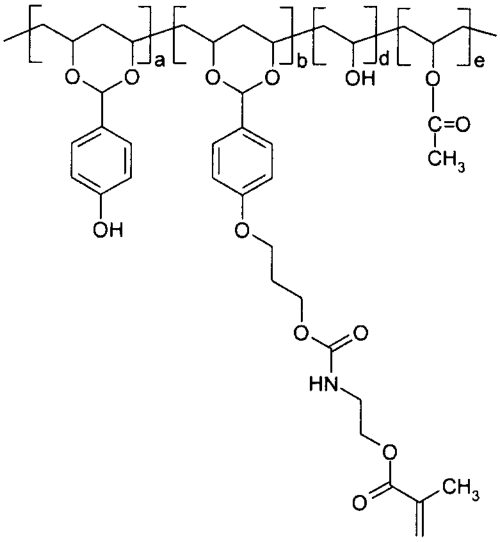

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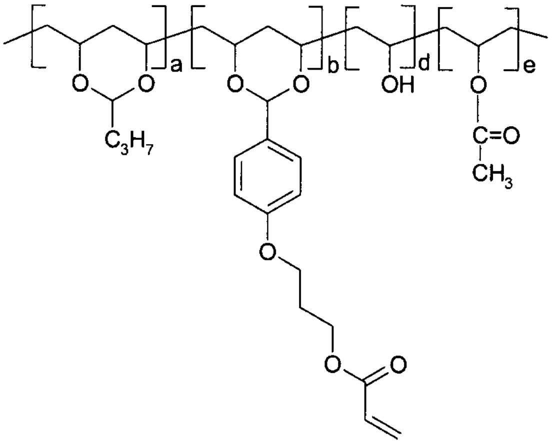

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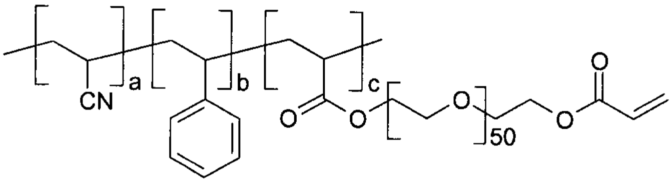

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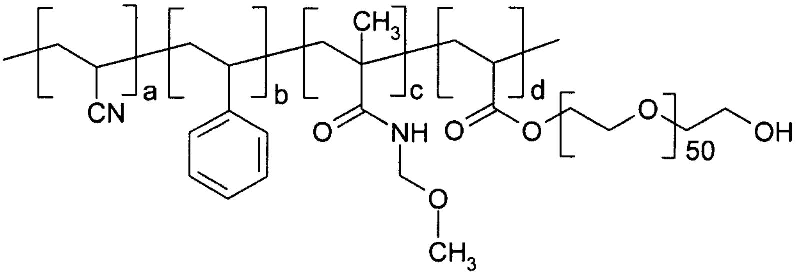


wherein a, b, c, d and e are molar ratios that may vary between about 0.01 and about 0.99.

67. Use of the coating solution of any one of Claims 19 to 66 in the preparation of a negative-working lithographic printing plate.

68. A negative working lithographic printing plate comprising a coating produced by depositing the coating solution of any one of Claims 19 to 66 onto a substrate.

69. The lithographic printing plate of Claim 68 wherein said coating weighs between about 0.5 and about 2.5 g/m^2.

70. The lithographic printing plate of Claim 68 or 69 comprising more than one coating according to any one of Claim 19 to 66.

71. The lithographic printing plate of any one of Claims 68 to 70 wherein said substrate is selected from the group consisting of anodized aluminum, plastic film, paper and combinations thereof.

72. The lithographic printing plate of Claim 71 wherein said anodized aluminum substrate has been brushed-grained or electro-grained before being anodized.

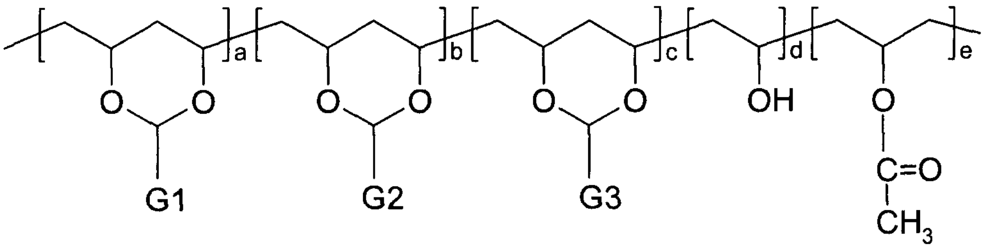
73. The lithographic printing plate of any one of Claims 68 to 72 wherein said lithographic printing plate further comprises a polymeric adhesion-promoting coating disposed between the substrate and the coating according to any one of claims 19 to 66.

74. The lithographic printing plate of Claim 73 wherein said polymeric adhesion-promoting coating comprises poly(acrylic acid) or poly(acrylic acid-co-vinylphosphoric acid).

75. The lithographic printing plate of Claim 73 or 74 wherein said polymeric adhesion-promoting coating weights between about 0.1 and about 1.0 g/m^2.

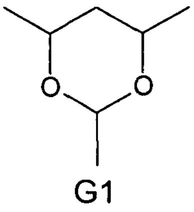
76. An acetal copolymer having attached thereto at least one functional group capable of undergoing cationic or radical polymerization.

77. The acetal copolymer of Claim 76 being:

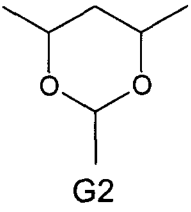


wherein:

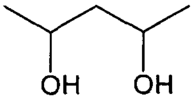
- G1 represents a processing segment providing solubility in organic solvents;
- G2 represents a thermal reactive segment;
- G3 represents a radiation-absorbing segment exhibiting one or more strong absorption bands between 700 and 1100 nm;
- a, b, c, d and e are molar ratios and may can vary from 0.01 to 0.99;
- any of



and



may independently be replaced by

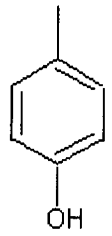


, and

- said functional group is attached to G2 or G3.

78. The acetal copolymer of Claim 77 wherein G3 further exhibit one or more strong absorption band between 400 and 700 nm.

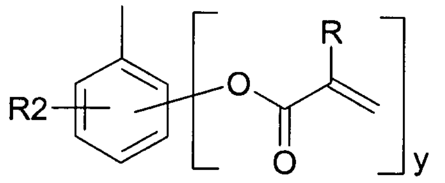
79. The acetal copolymer of Claims 77 or 78 wherein G1 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl comprise a cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide methylbenzylsufonyl-carbamat, carboxylic acid or phosphoric acid functional group.

80. The acetal copolymer of Claim 79 wherein G1 is  .

81. The acetal copolymer of any one of Claims 77 to 80 wherein G2 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl has attached thereto said functional group.

82. The acetal copolymer of Claim 81 wherein said functional group is vinyl ether, alkoxy-methyl acrylamide or alkoxy methacrylamide.

83. The acetal copolymer of Claim 82 wherein G2 is: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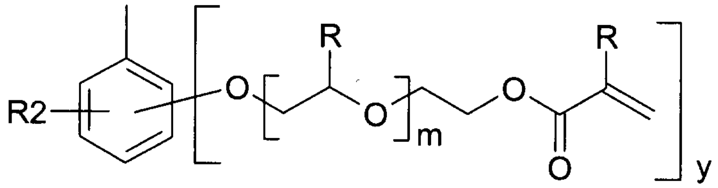
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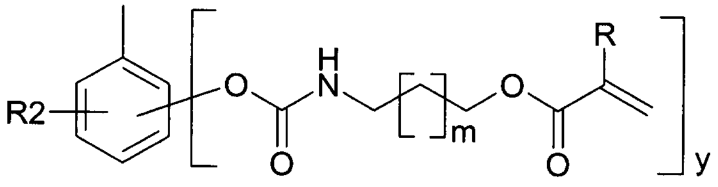
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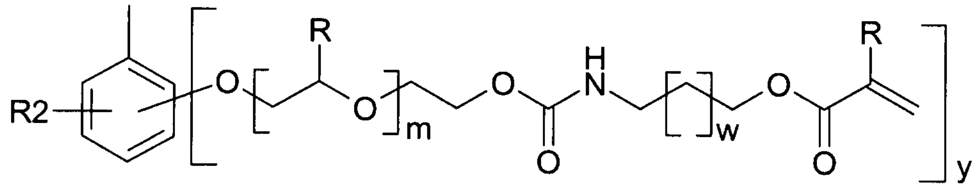
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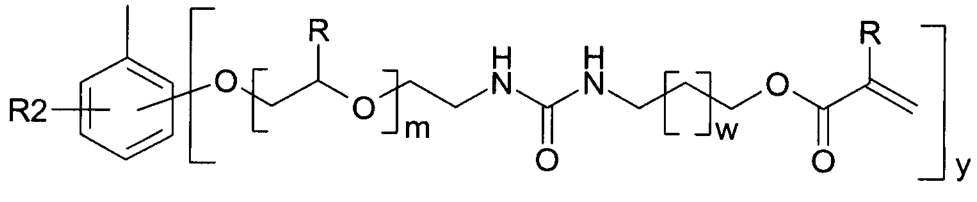
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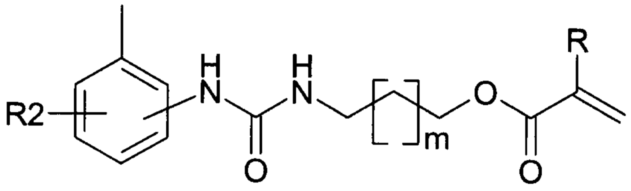
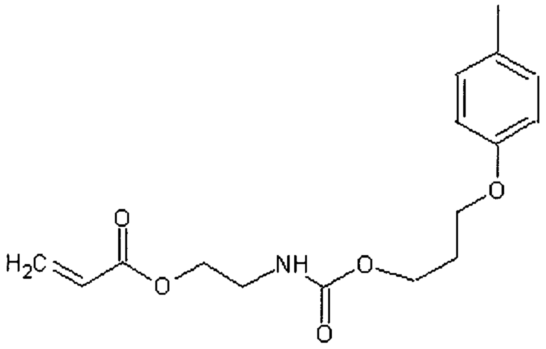


wherein:

- R is hydrogen or methyl;
- R2 is C1 – C8 alkyl or alkoxy;
- m and w may vary between 0 and 50; and
- y is 1 or 2.

84. The acetal copolymer of Claim 82 where G2 is:



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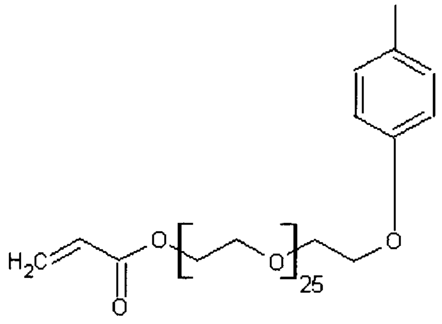

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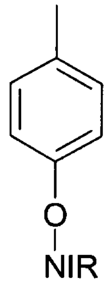
85. The acetal copolymer of any one of Claims 77 to 84 wherein the acetal copolymer comprises more than one G3 segments that may be identical to or different from each other.

86. The acetal copolymer of any one of Claims 77 to 85 wherein G3 is



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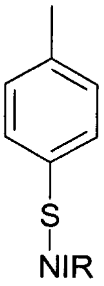
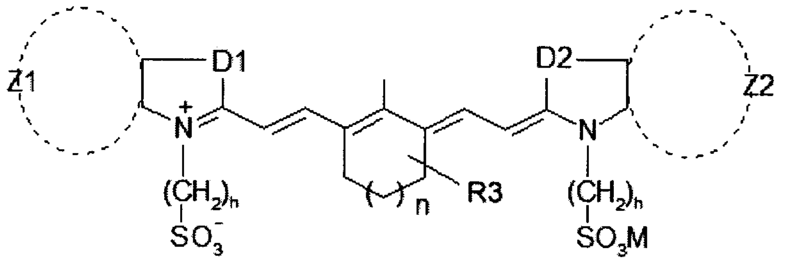


, wherein NIR is a near-infrared absorbing chromophore exhibiting one or more strong absorption peaks between 700 and 1100 nm.

87. The acetal copolymer of Claim 86 wherein said near-infrared absorbing chromophore is:



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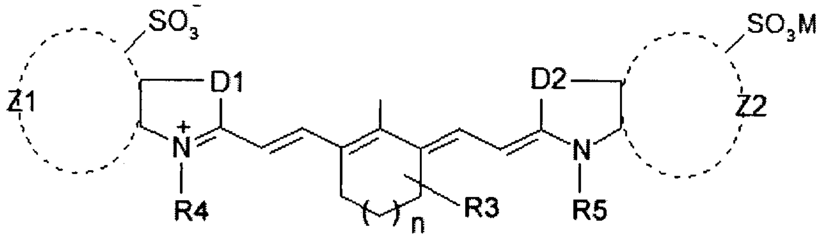

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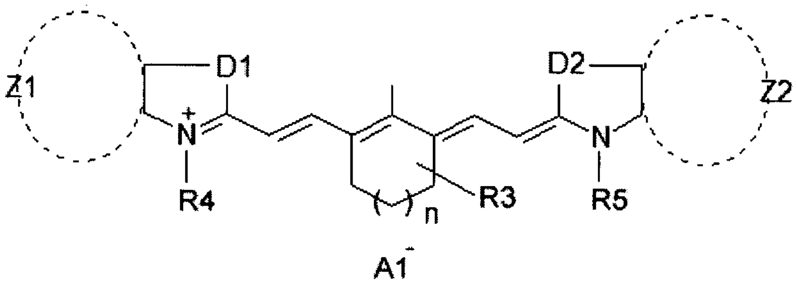

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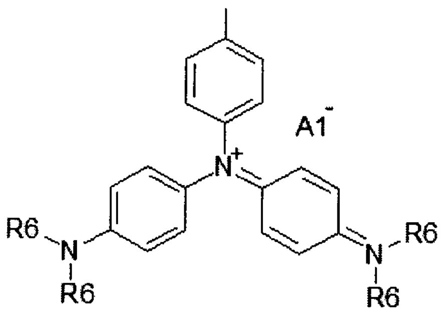

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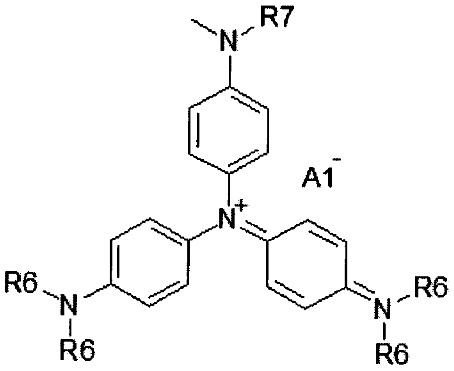
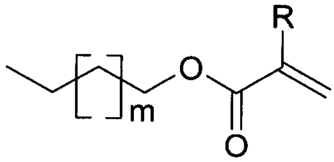


wherein:

- D1 and D2 are independently –O-, -S-, -Se-, -CH = CH-, and -C(CH3)2;
- Z1 and Z2 each independently represent one or more fused substituted or unsubstituted aromatic ring;
- h may vary from 2 to 8;
- n represents 0 or 1;
- M represents hydrogen or Na, K, or tetraalkylammonium salts cationic counter ion.
- A1 represents bromide, chloride, iodide, tosylate, triflate, trifluoromethane carbonate, dodecyl benzosylfonate and tetrafluoroborate, tetraphenylborate or triphenyl-n-butylborate anionic counter ion.
- R3 and R7 each independently represent hydrogen or alkyl;
- R4, R5 and R6 each independently represent alkyl, aryl alkyl, hydroxy alkyl, amino alkyl, carboxy alkyl, sulfo alkyl or a polymerizable substituent, said substituent comprising said functional group and being of formula:



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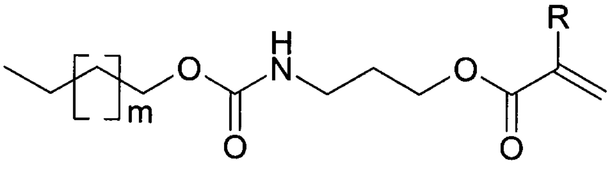

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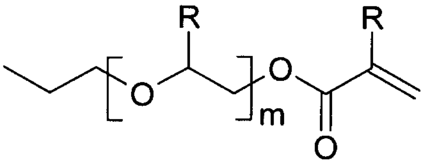

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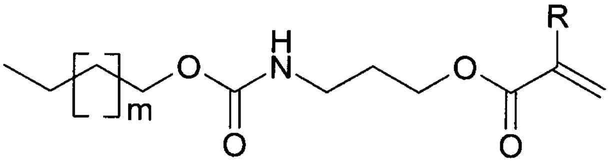
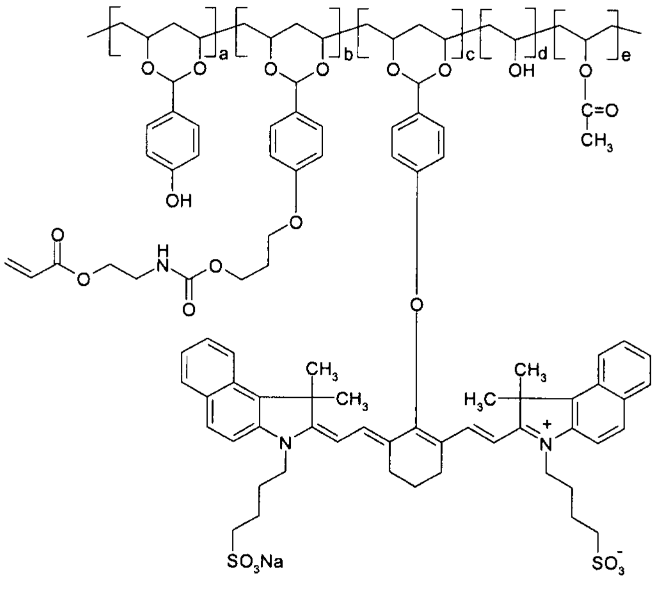
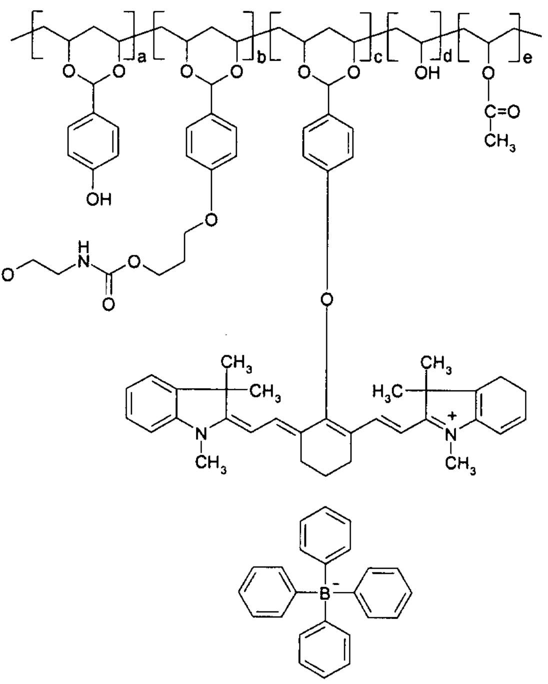


wherein m may vary between 0 and 50 and R is hydrogen or methyl.

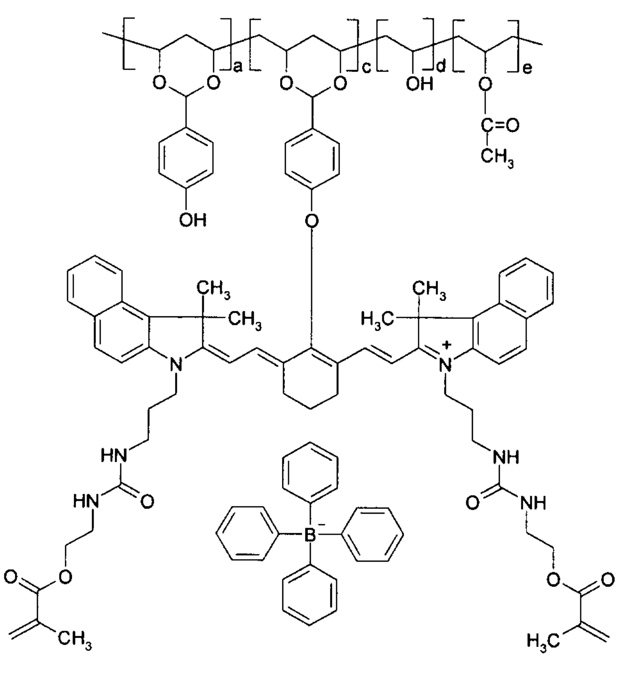
88. The acetal copolymer of Claim 87 wherein at least one of Z1 of Z2 is phenyl or naphtyl.

89. The acetal copolymer of Claim 88 being of formula:




a
b
c
d
e
OH
OH
C=O
CH3
O
H
N
O
CH3
CH3
H3C
N
N
+
B
-

,


a
c
d
e
OH
OH
C=O
CH3
O
CH3
CH3
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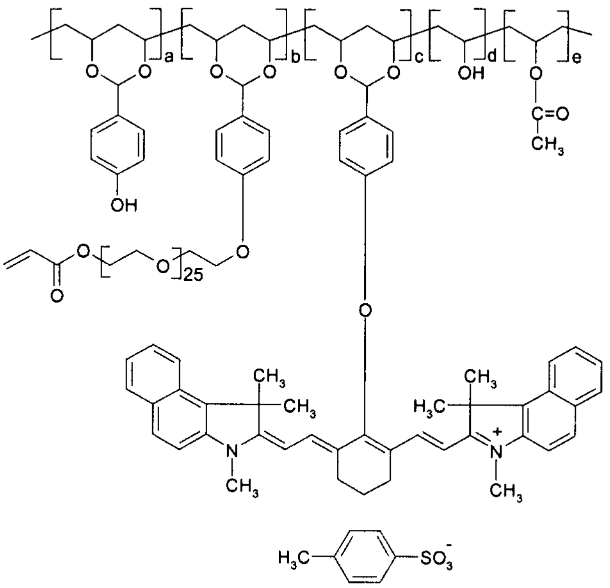
, or



wherein a, b, c, d and e are molar ratios that may vary from 0.01 to 0.99.

90. Use of the acetal copolymer of any one of Claims 76 to 89 or a mixture thereof in the preparation of a coating.

91. The use of Claim 90 wherein the coating is a negative working lithographic printing plate coating.

92. A lithographic printing plate coating solution comprising the acetal copolymer of any one of Claims 76 to 89 or a mixture thereof.

93. The coating solution of Claim 92 comprising from about 5% to about 50 % by solid weight of said acetal copolymer.

94. The coating solution of Claim 92 or 93 further comprising an iodonium salt according to any one of Claims 1 to 13

95. The coating solution of any one of Claims 92 to 94 further comprising a polymer binder.

96. The coating solution of Claim 95 wherein said polymer binder is as defined in any one of Claims 41 to 57.

97. Use of the coating solution of any one of Claims 92 to 96 in the preparation of a negative-working lithographic printing plate.

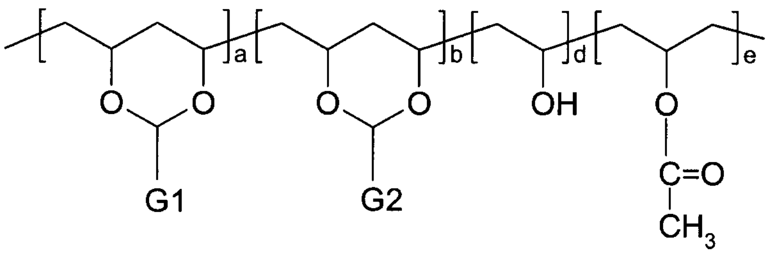
98. A negative working lithographic printing plate comprising a coating produced by depositing the coating solution of any one of Claims 92 to 96 onto a substrate.

99. A polymer binder for lithographic printing plate coatings having attached thereto at least one functional group capable of undergoing cationic or radical polymerization.

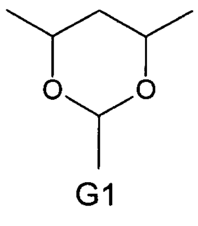
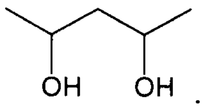
100. The polymer binder of Claim 99 wherein said functional group is acrylate, methacrylate, vinyl ether, hydroxyl, alkoxy-methyl acrylamide, alkoxy methacrylamide, N-methoxymethylacrylamide or N-methoxymethylmethacrylamide.

101. The polymer binder of Claim 99 or 100 being an acetal copolymer or a mixture thereof.

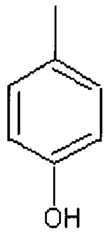
102. The polymer binder of Claim 101 having the following structure:



wherein

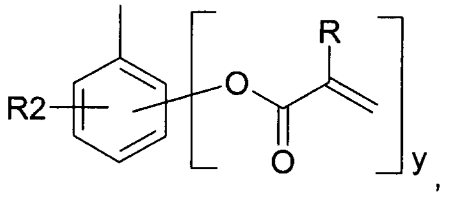
- G1 represents an processing segment providing solubility in organic solvents;
- G2 represents an thermal reactive segment having attached thereto said functional group;
- a, b, d and e are molar ratios and may vary from 0.01 to 0.99; and
-  may be replaced by  .

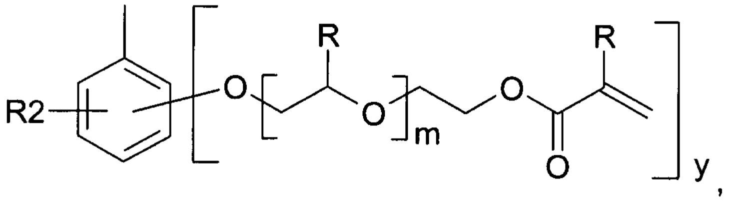
103. The polymer binder of Claim 102 wherein G1 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl comprise a cyano, hydroxy, dialkylamino, trialkylammonium salts, ethylene oxide, propylene oxide methylbenzylsufonyl-carbamat, carboxylic acid and phosphoric acid functional group.

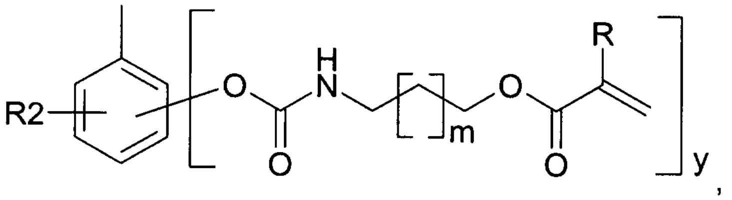
104. The polymer binder of Claim 102 wherein G1 is C_3H_7 or  .

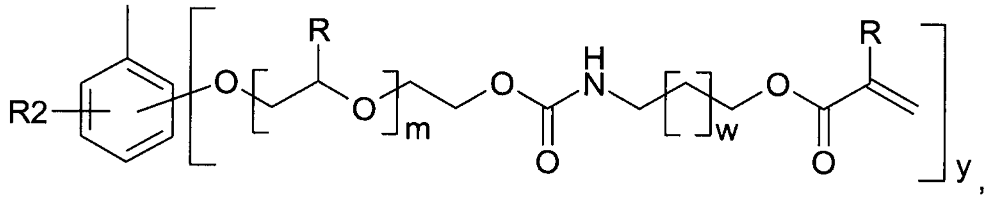
105. The polymer binder of any one of Claims 102 to 104 wherein G2 is linear alkyl, branched alkyl, linear aryl or branched aryl, wherein said linear alkyl, branched alkyl, linear aryl or branched aryl has attached thereto said functional group.

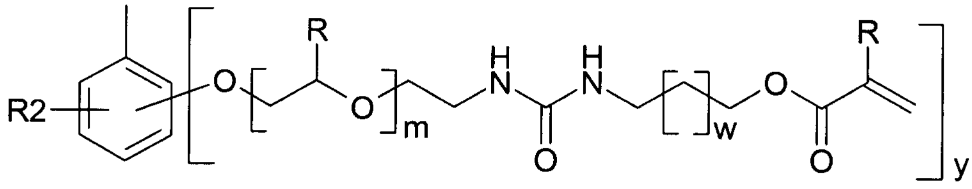
106. The polymer binder of Claim 105 wherein G2 is:

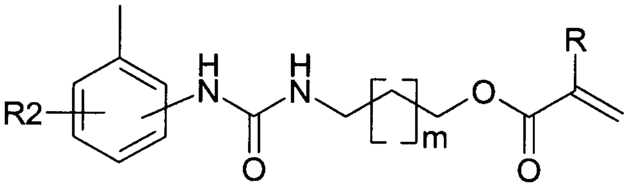








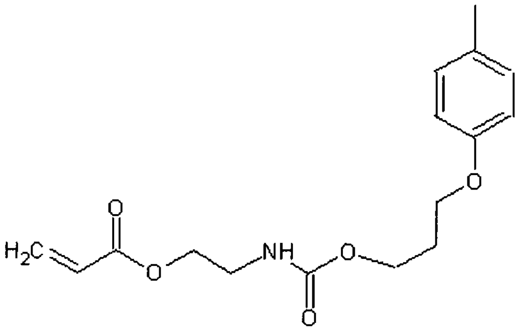
 , or



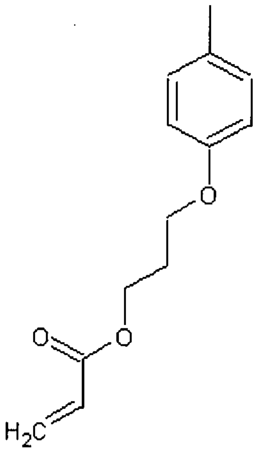
wherein:

- R is hydrogen or methyl;
- R2 is C1 – C8 alkyl or alkoxy;
- m and w may vary between 0 and 50; and
- y is 1 or 2.

107. The polymer binder of Claim 105 wherein G2 is:

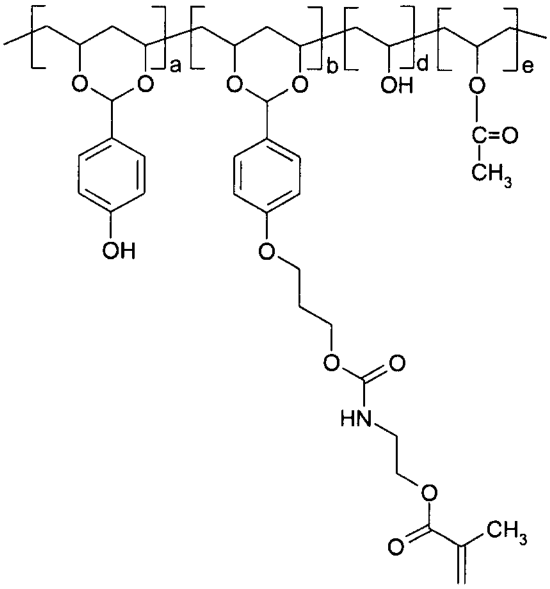


or



.

108. The polymer binder of Claim 107 having the formula:



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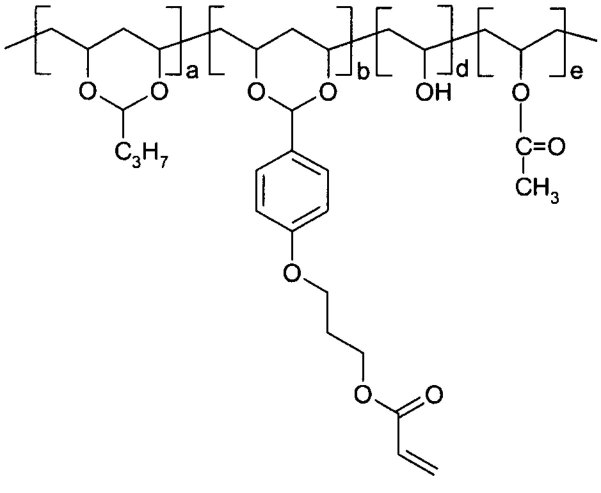
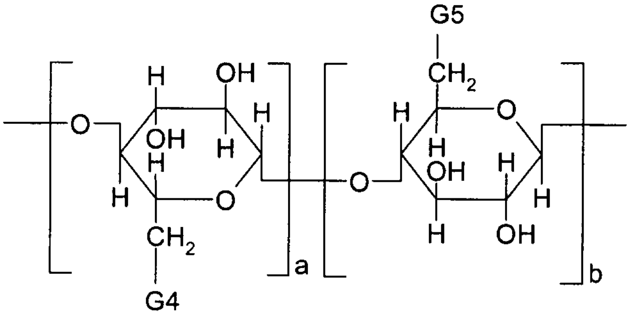


.

109. The polymer binder of Claim 99 or 100 being a solvent-soluble cellulose ether, a water-soluble cellulose ether or a mixture thereof, said cellulose ethers having attached thereto said functional group.

110. The polymer binder of Claim 109 wherein said cellulose ethers have been modified by reacting a hydroxymethyl, a hydroxyethyl or a hydroxypropyl group attached to said cellulose ethers with a 2-isocyanato-ethyl compound having attached thereto said functional group.

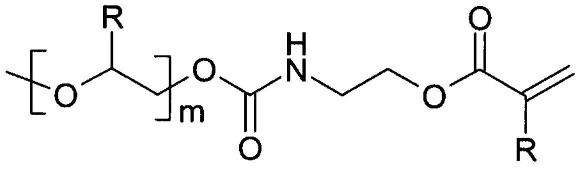
111. The polymer binder of Claim 109 or 110 having the following structure:



wherein:

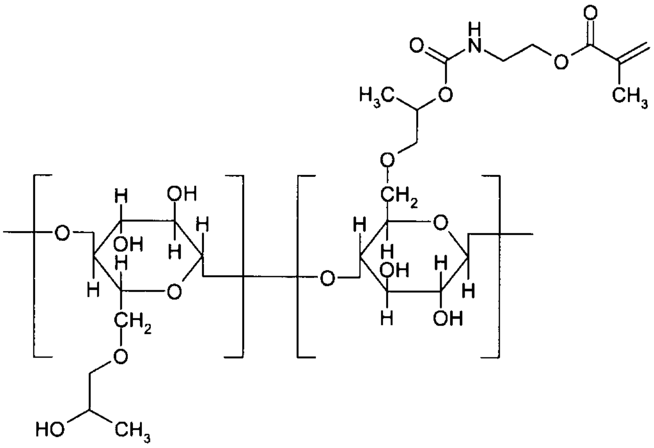
- a and b are molar ratios and may vary between about 0.01 and about, 0.99,
- G4 is hydroxy, hydroxyethyl or hydroxypropyl; and
- G5 comprises said functional group.

112. The polymer binder of Claim 111 wherein G5 is



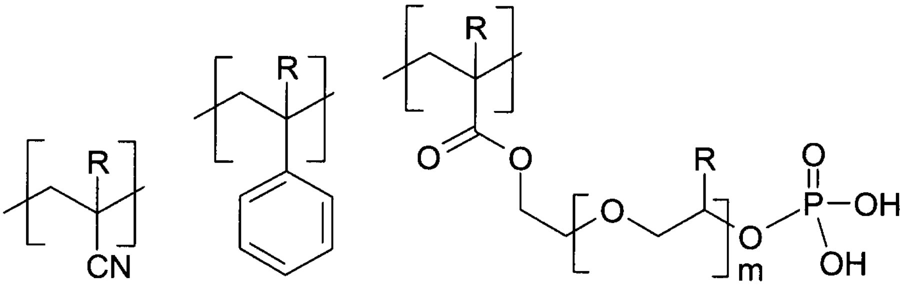
wherein m is 0 or 1 and R is hydrogen or methyl.

113. The polymer binder of Claim 112 having the following structure:



.

114. The polymer binder of Claim 99 or 100 being a copolymer comprising one or more first monomers of formula:



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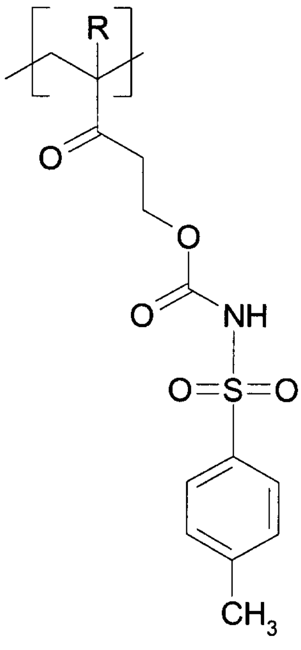

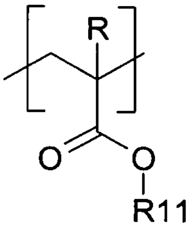

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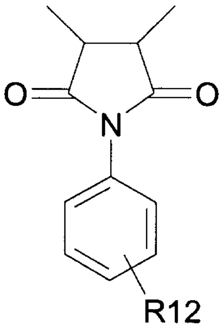
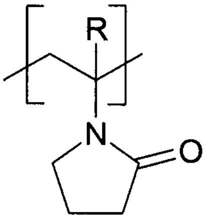
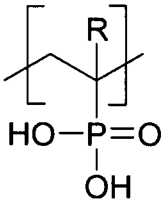
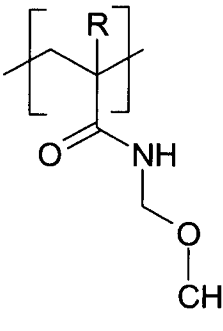




, or



and one or more second monomers of formula:



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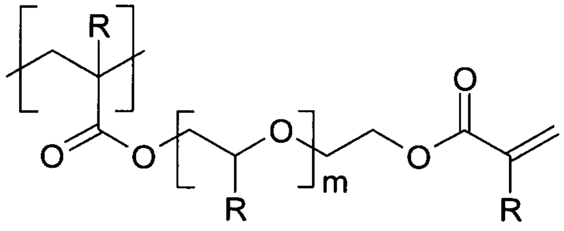

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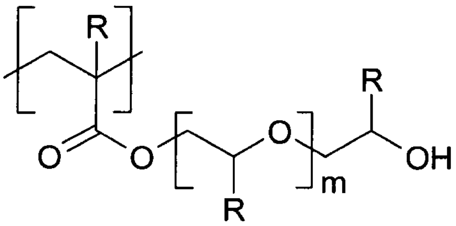

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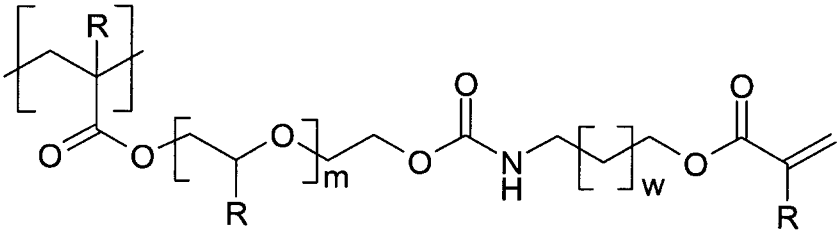

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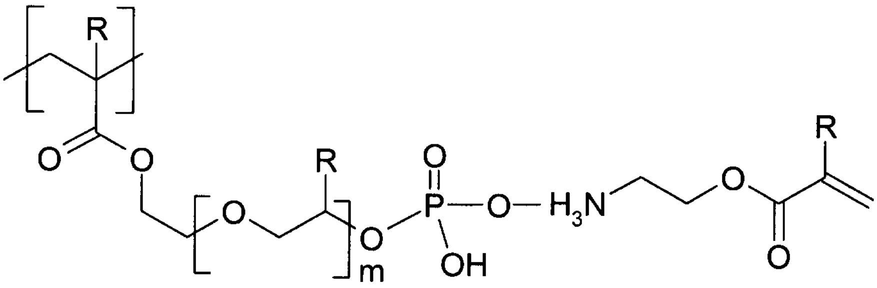
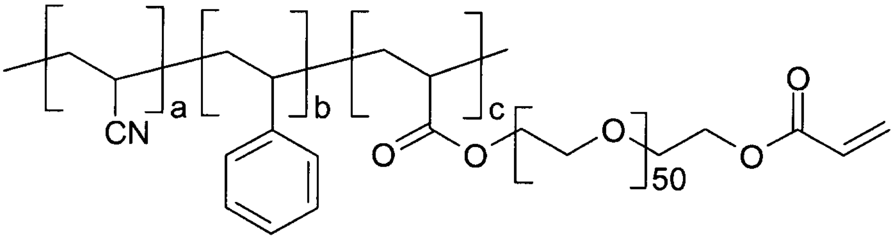


wherein:

- m and w may vary between 0 and 50;
- R is hydrogen or methyl;
- R11 is linear or branched alkyl chain; and
- R12 is alkyl, hydroxyl or carboxylic acid.

115. The polymer binder of Claim 114 being:



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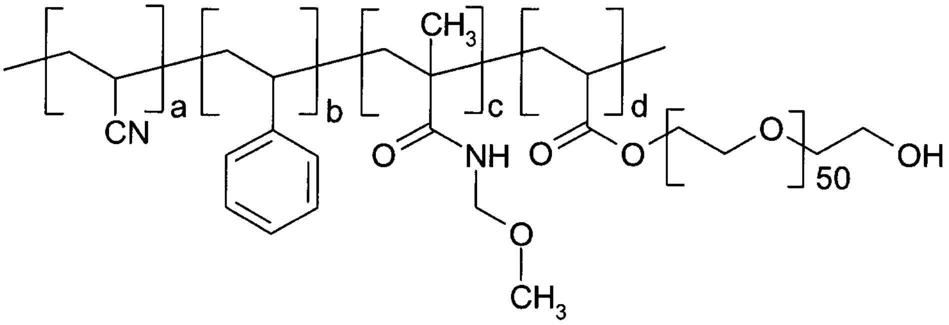

,

wherein a, b, c and d are molar ratios and may vary between about 0.01 and about 0.99.

116. Use of the polymer binder of any one of Claims 99 to 115 or a mixture thereof

in the preparation of a coating.

117. The use of Claim 116 wherein the coating is a negative working lithographic printing plate coating.

118. A lithographic printing plate coating solution comprising the polymer binder of any one of Claims 99 to 115 or a mixture thereof.

119. The coating solution of Claim 118 comprising from about 1% to about 50 % by solid weight of said polymer binder.

120. The coating solution of Claim 118 or 119 further comprising an iodonium salt according to any one of Claims 1 to 13

121. The coating solution of any one of Claims 118 to 120 further comprising a near infrared absorbing dye.

122. The coating solution of Claim 121 wherein said near infrared absorbing dye is as defined in any one of claims 22 to 38.

123. Use of the coating solution of any one of Claims 118 to 122 in the preparation of a negative-working lithographic printing plate.

124. A negative working lithographic printing plate comprising a coating produced by depositing the coating solution of any one of Claims 118 to 122 onto a substrate.

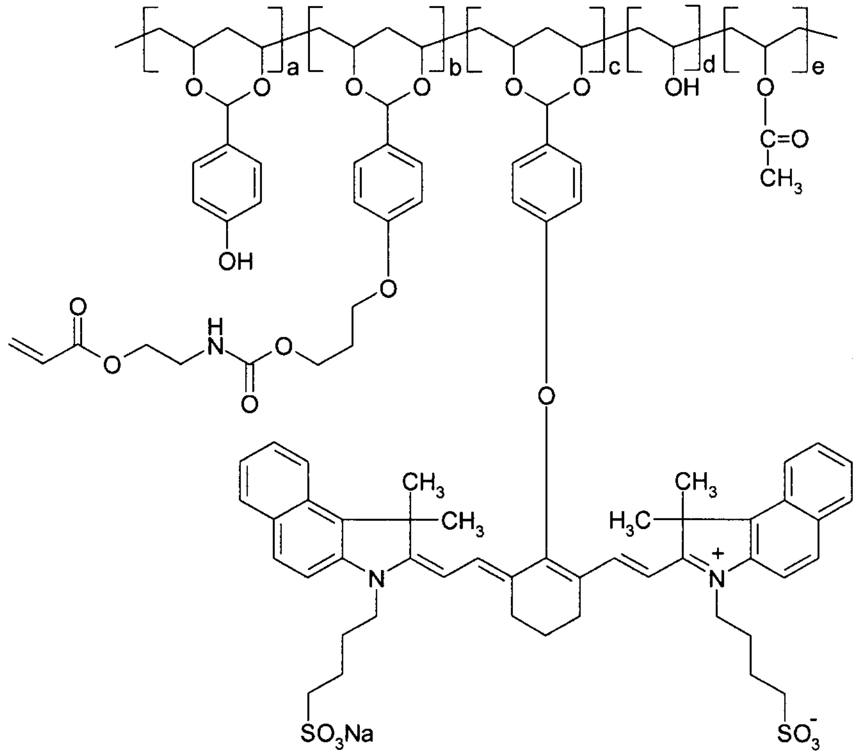

Figure 1

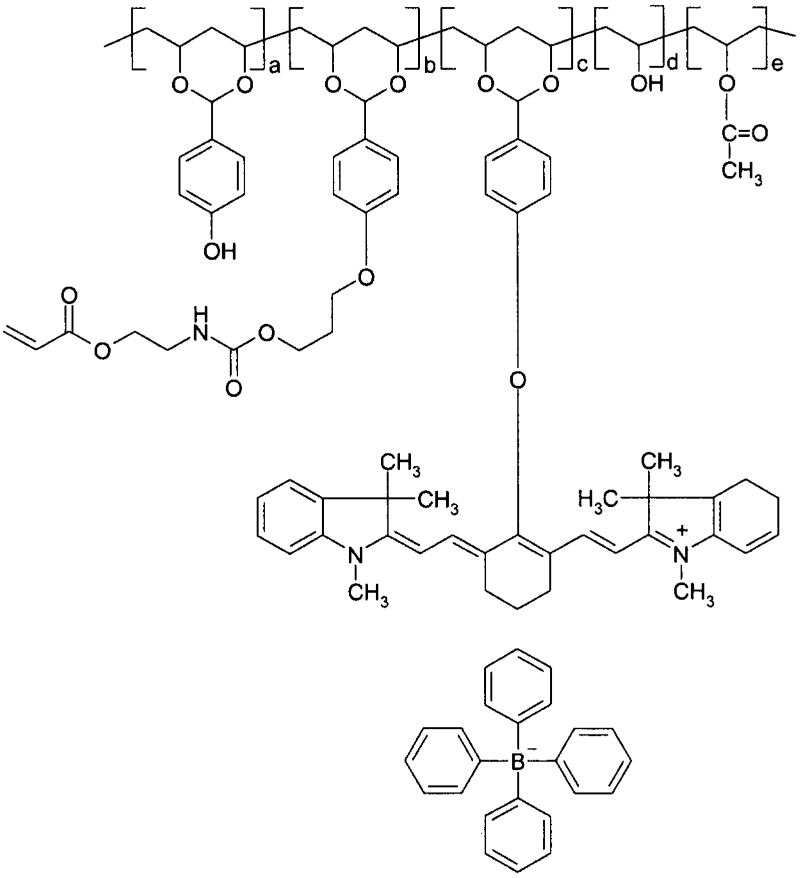

Figure 2

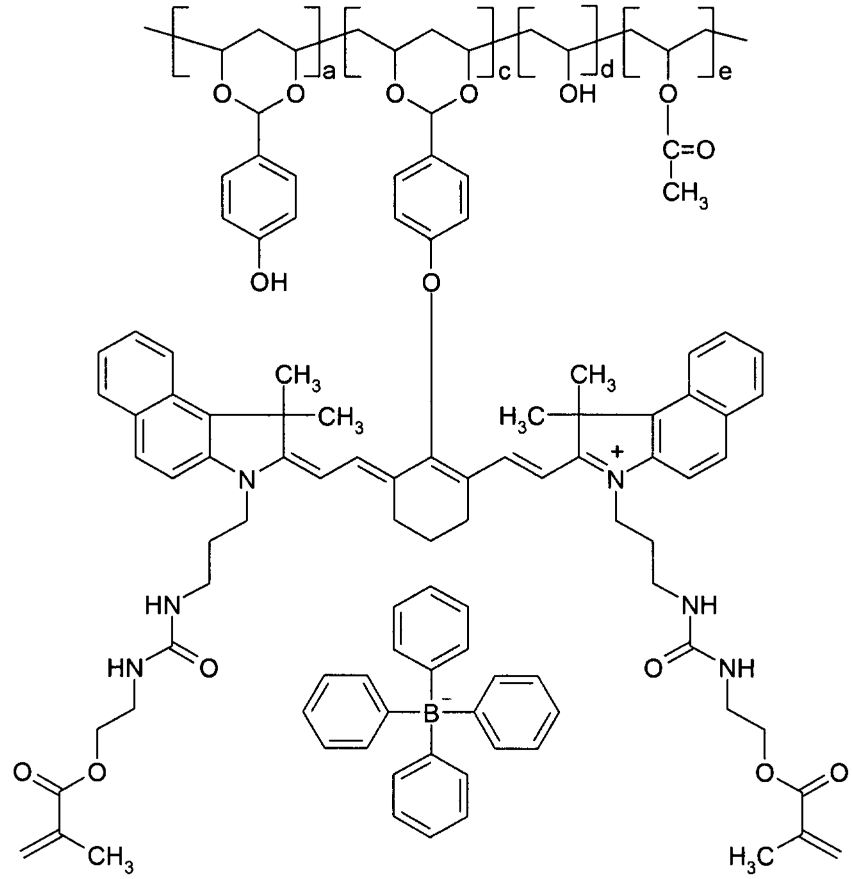
a
c
d
e
O
O
O
O
OH
O
C=O
CH$_3$
OH
O
CH$_3$
CH$_3$
N
CH$_3$
H$_3$C
N
+
HN
HN
O
O
O
CH$_3$
B
−
NH
O
NH
O
O
H$_3$C

Figure 3

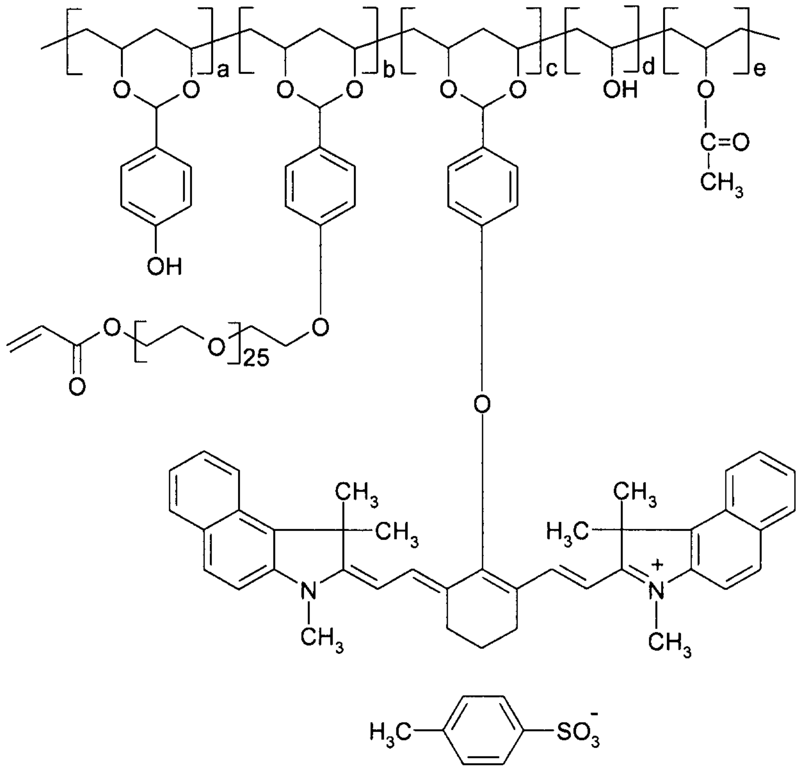

Figure 4

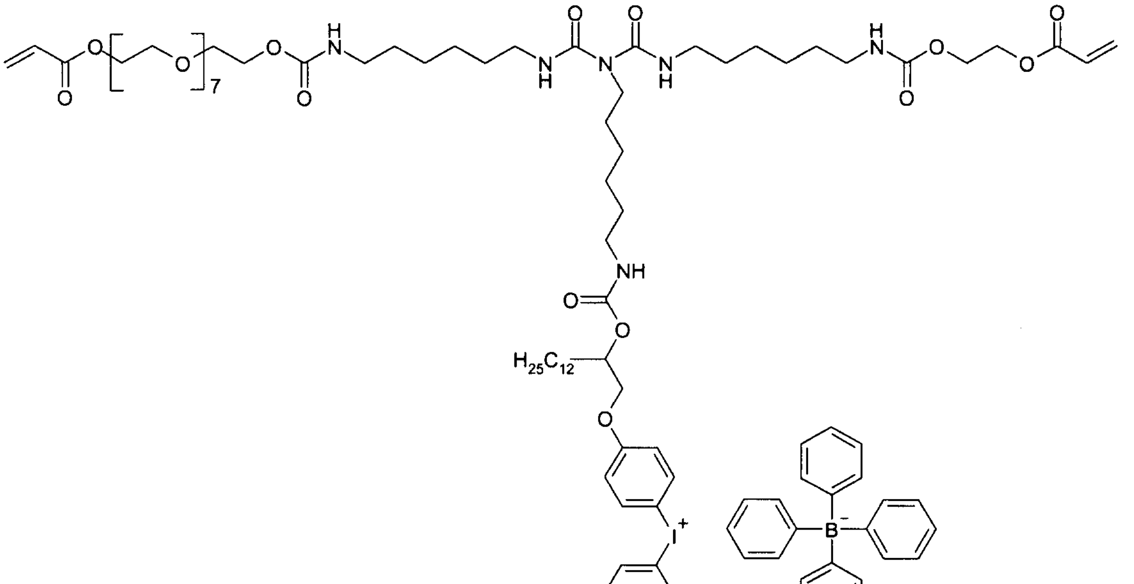

Figure 5

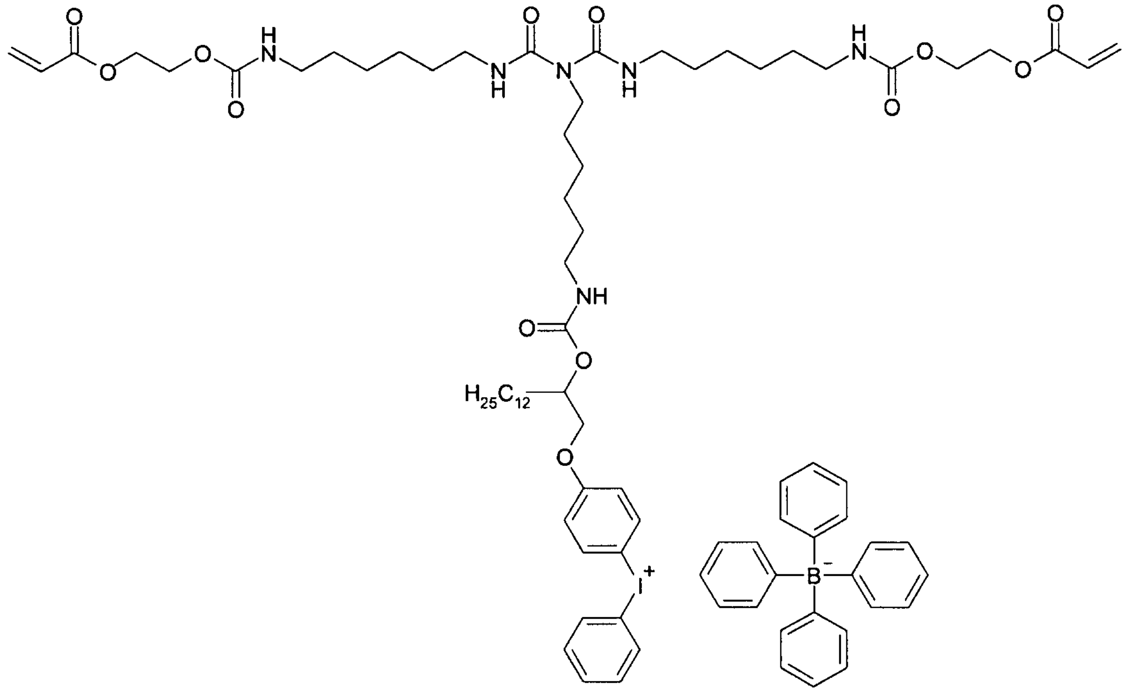

Figure 6

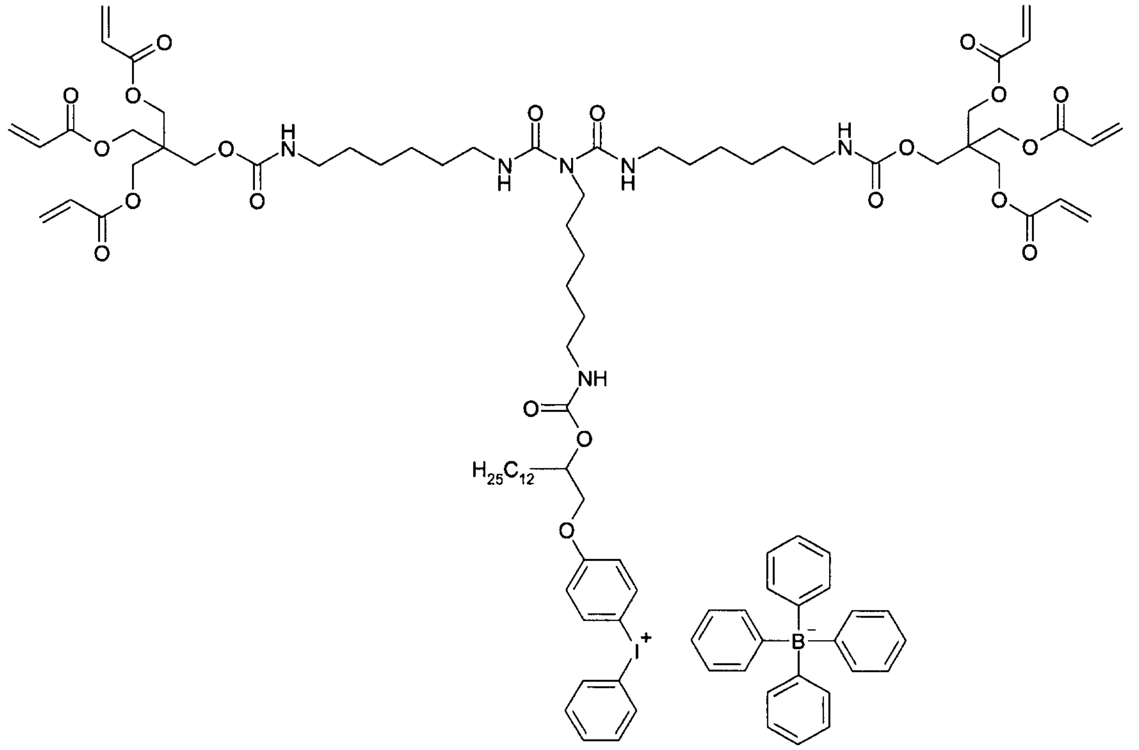

Figure 7

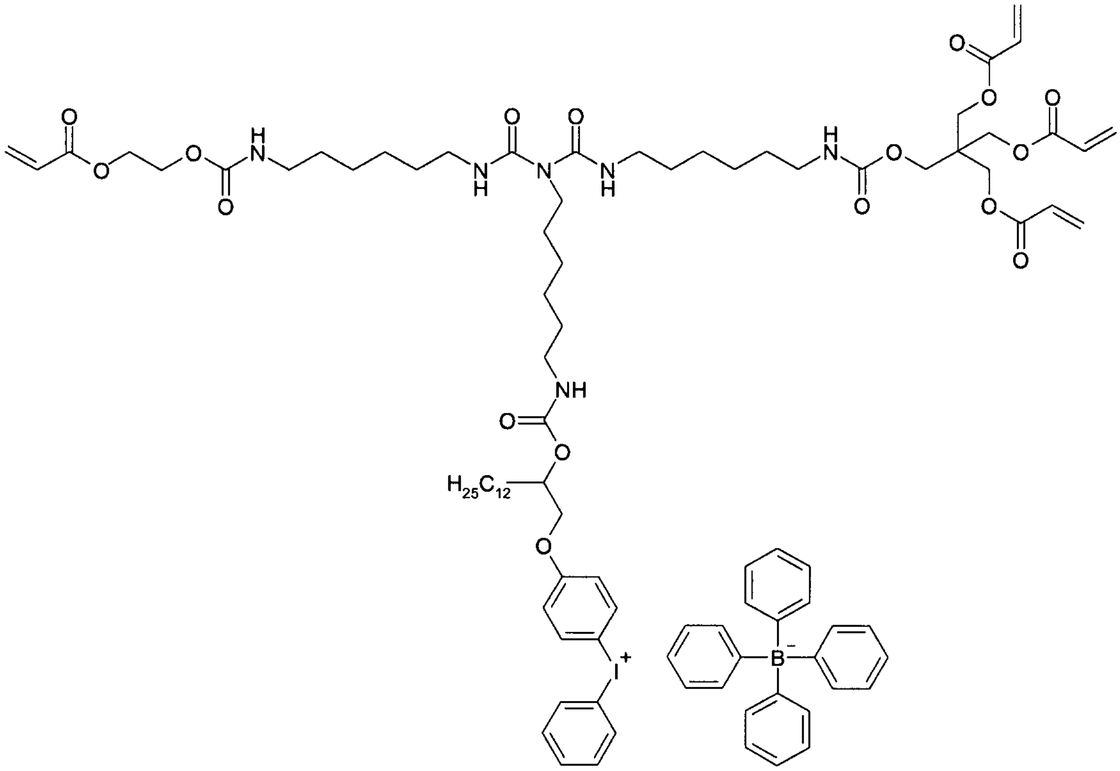

Figure 8

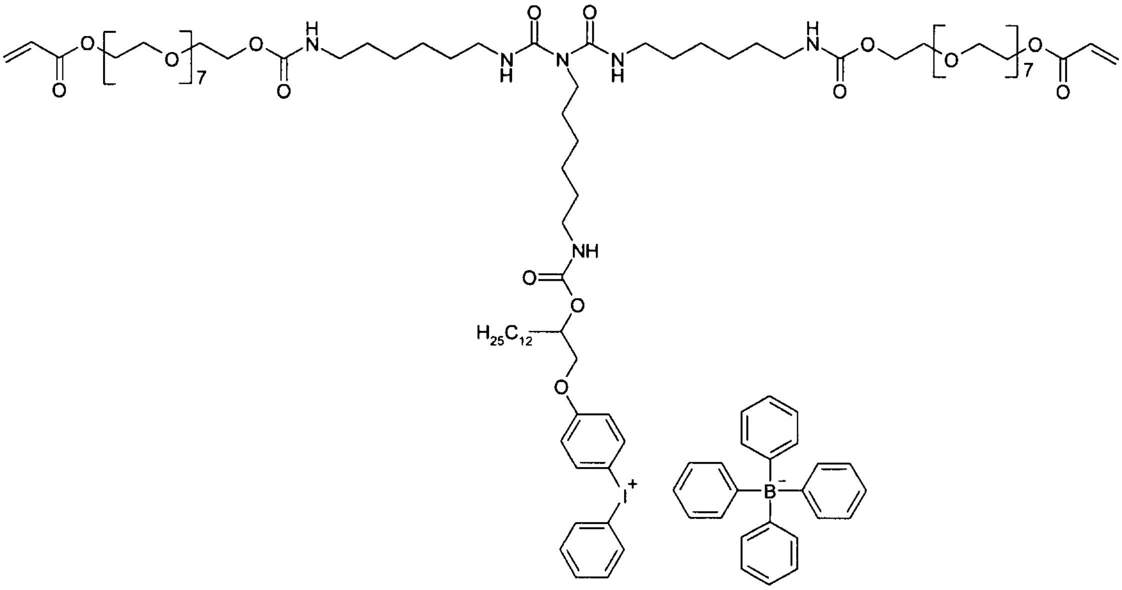

Figure 9

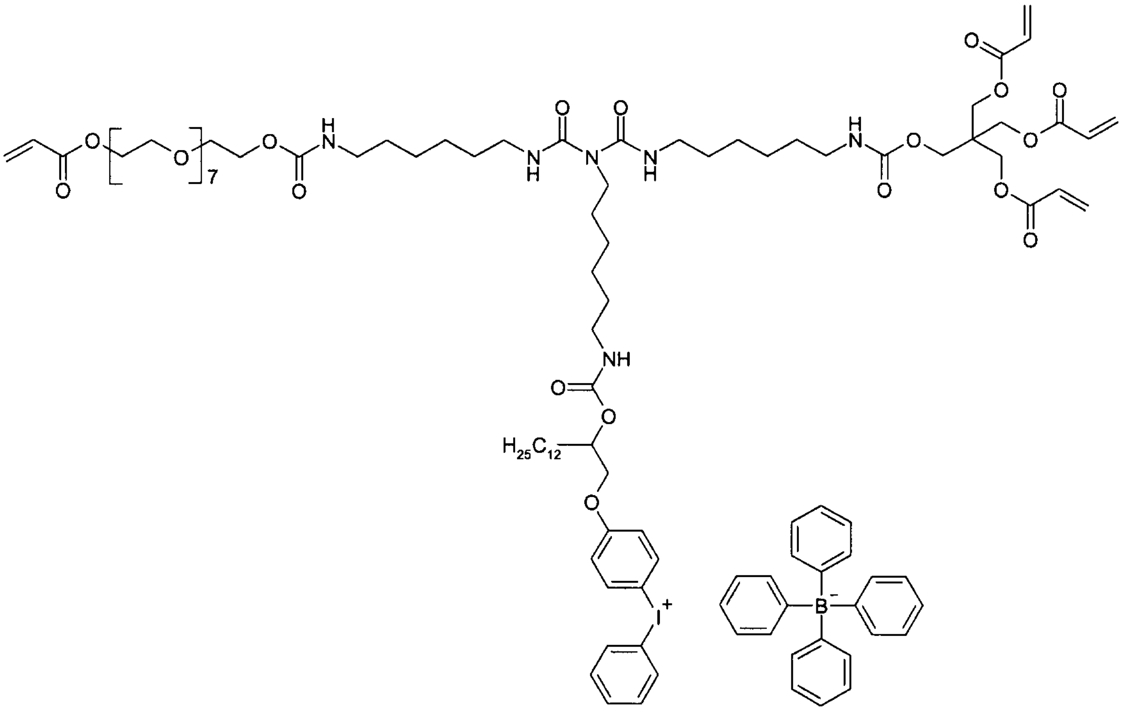

Figure 10

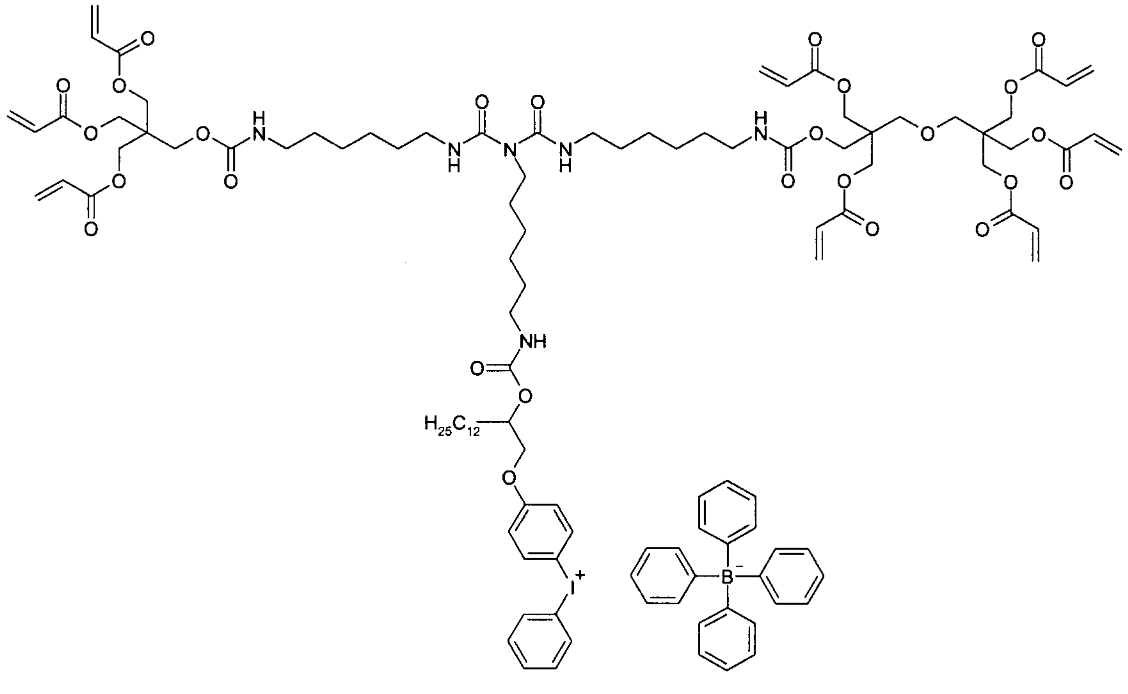

Figure 11

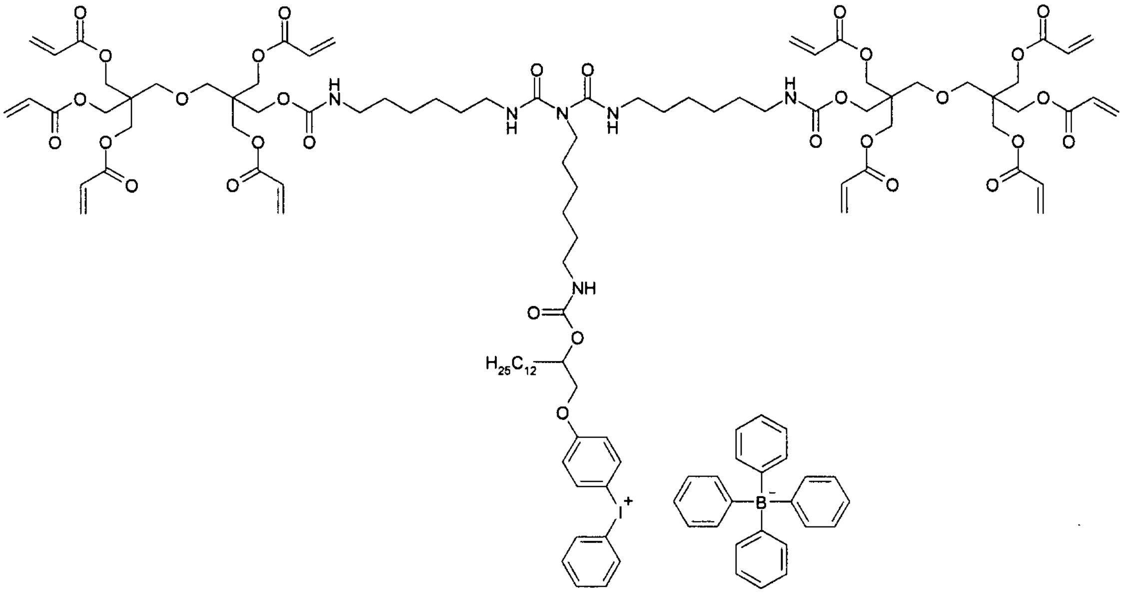

Figure 12

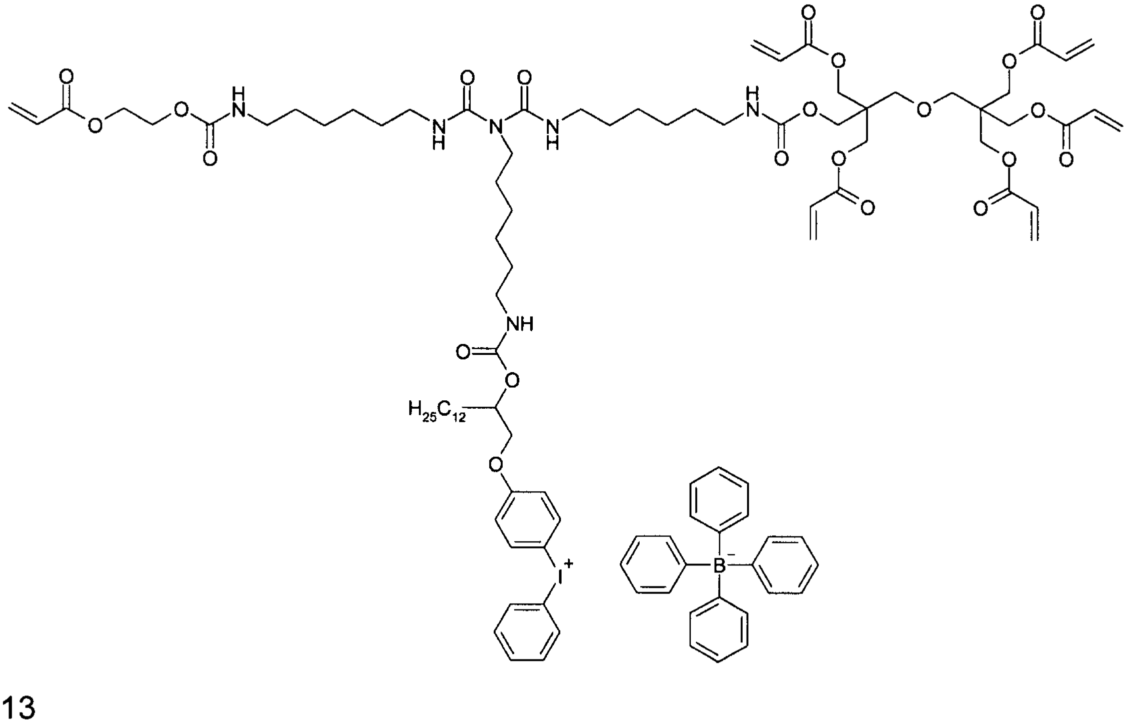

Figure 13

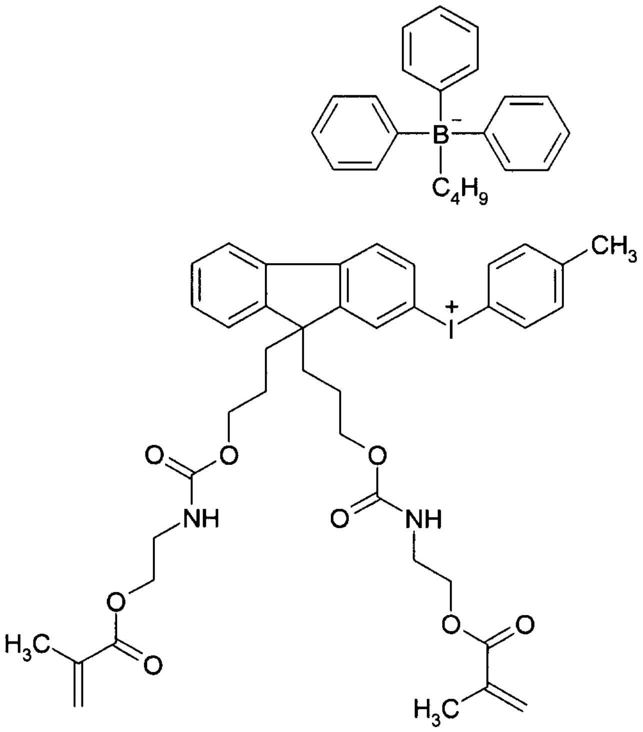

Figure 14

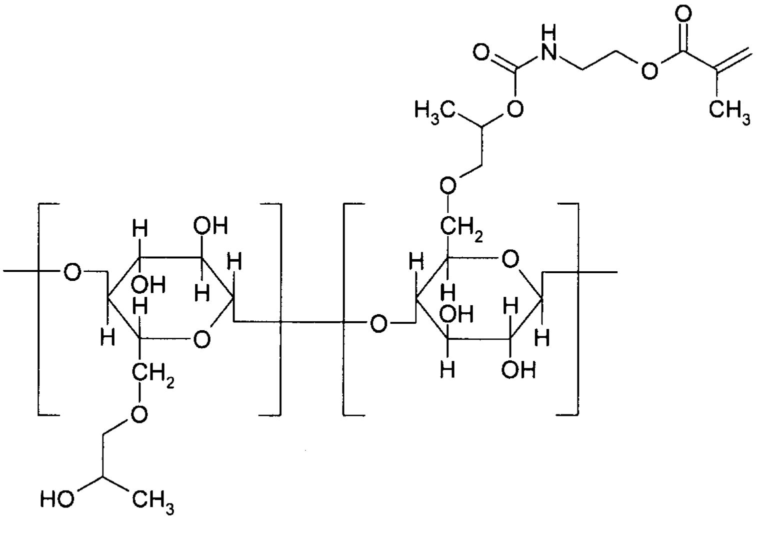

Figure 15

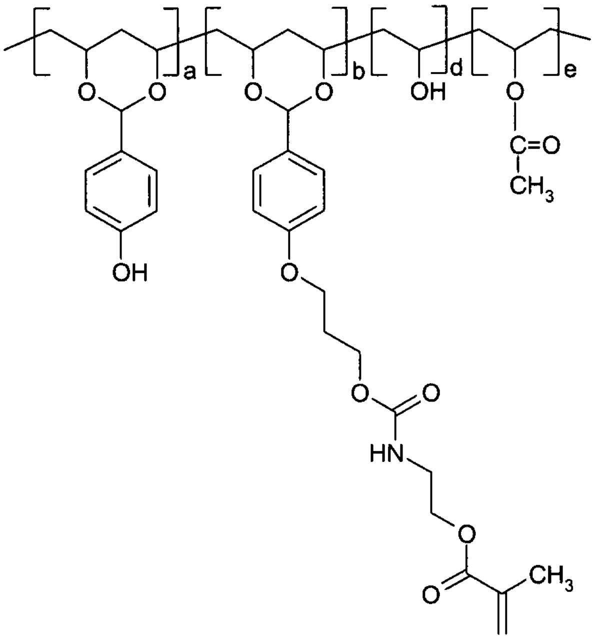

Figure 16

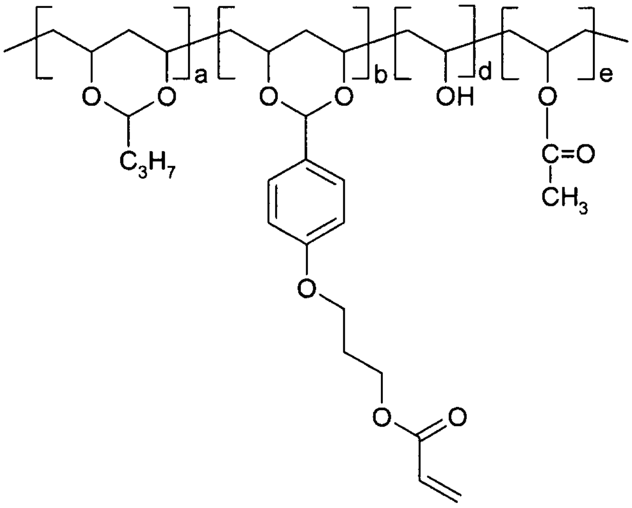

Figure 17

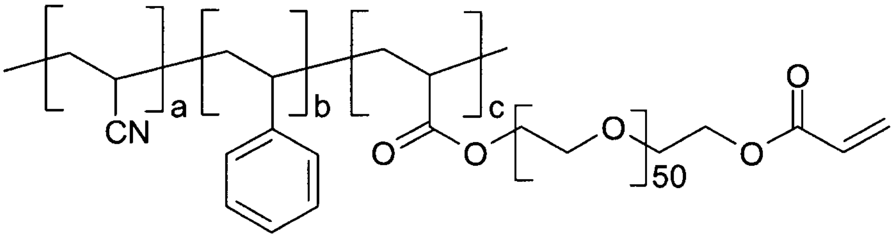

Figure 18

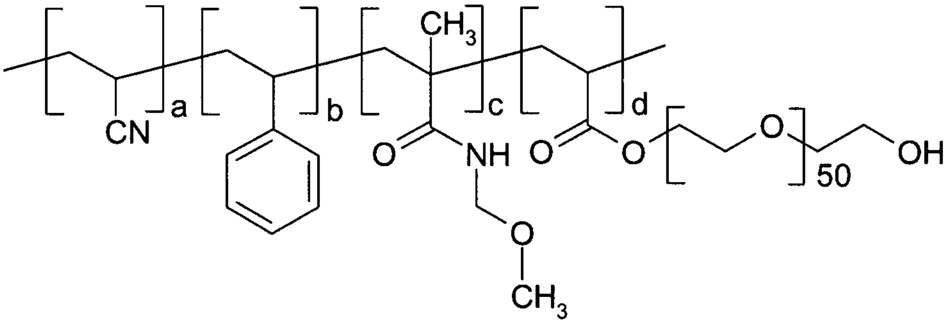

Figure 19

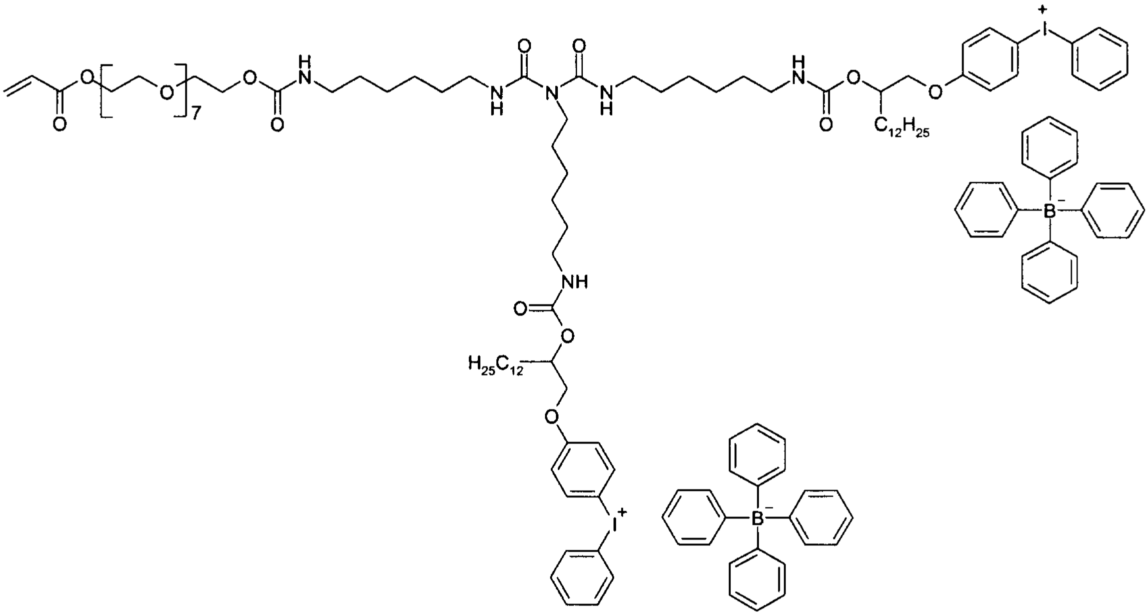

Figure 20

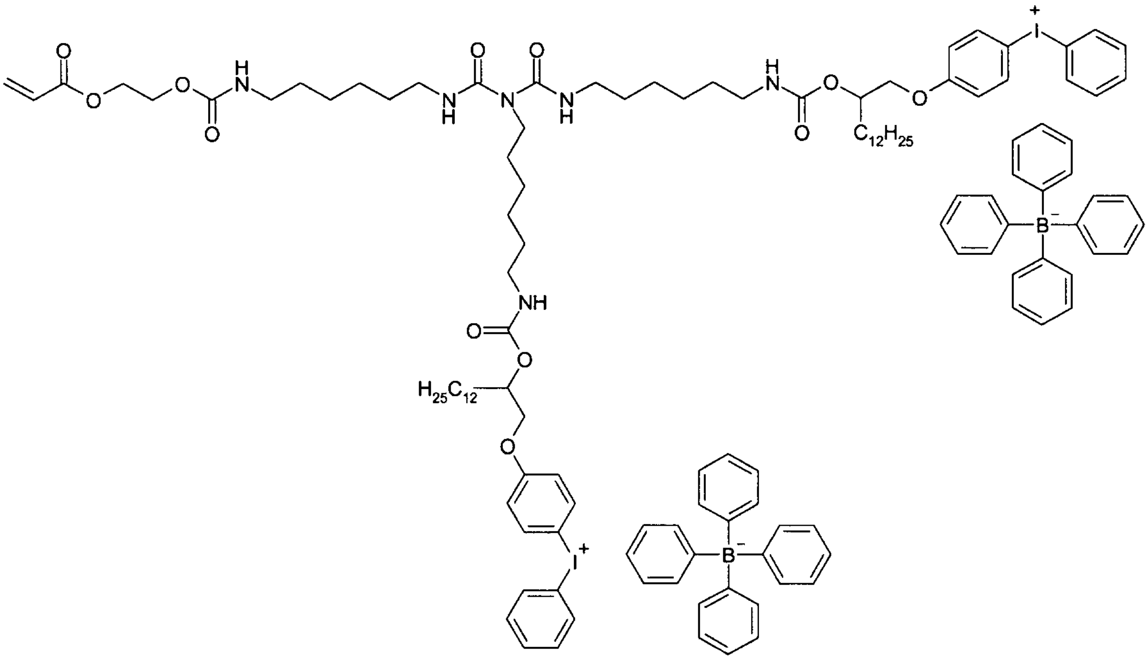

Figure 21

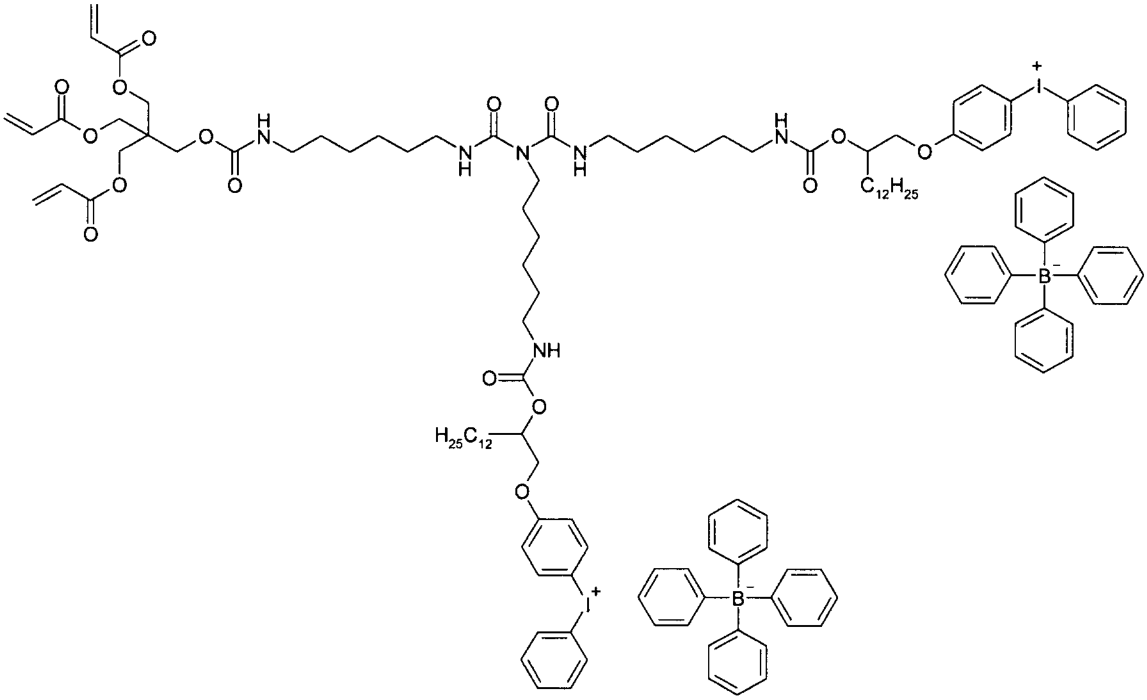

Figure 22

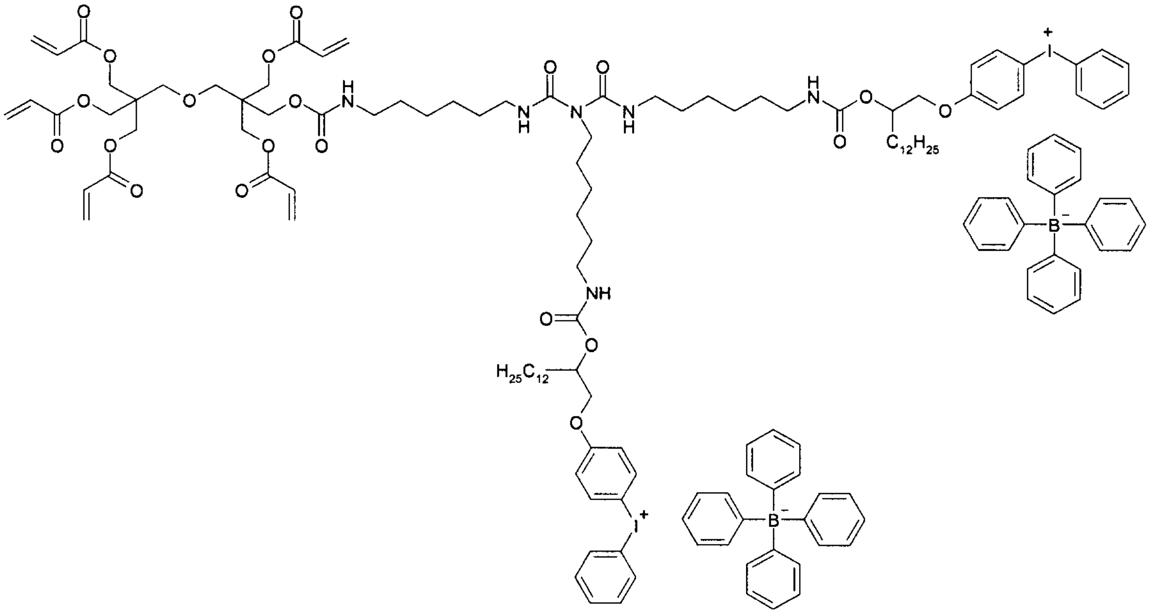

Figure 23

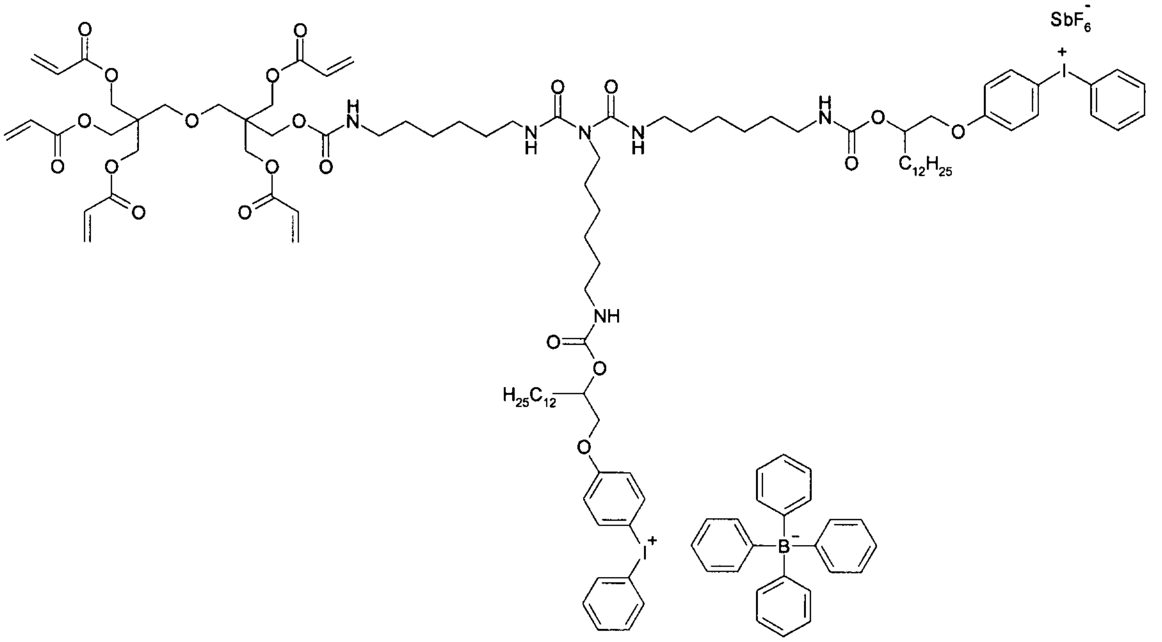

Figure 24

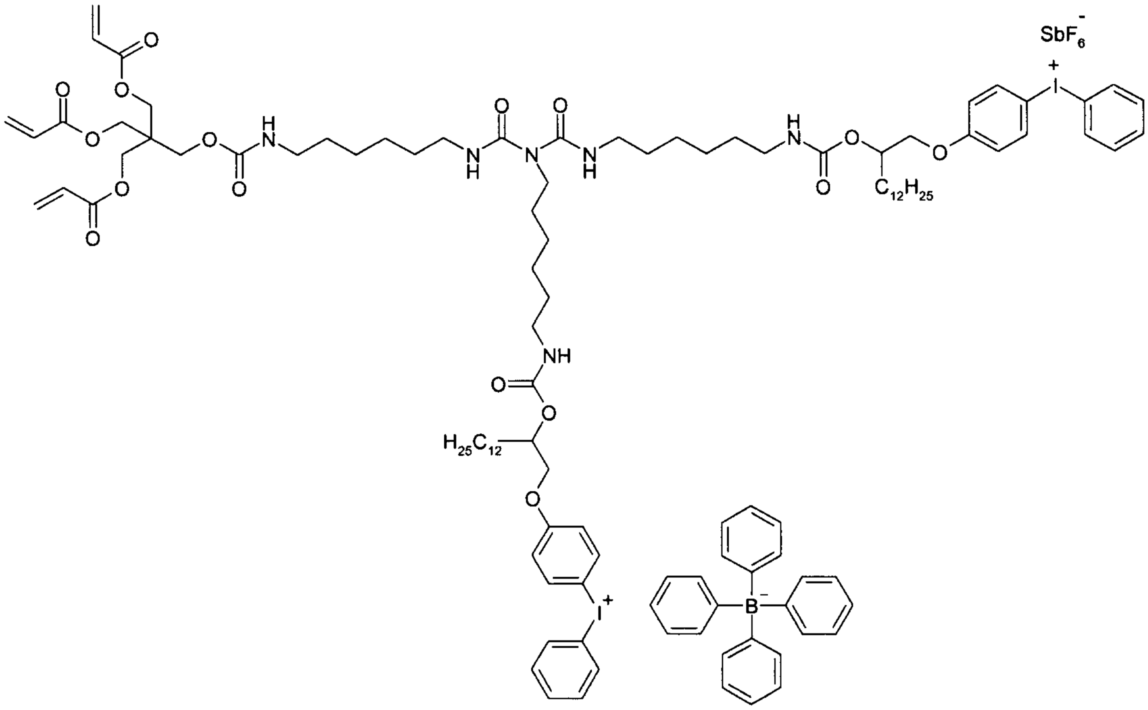

Figure 25

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2007/000820

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07C 275/62*** (2006.01), ***B41C 1/10*** (2006.01), ***B41N 1/14*** (2006.01), ***C07C 271/08*** (2006.01), ***C07F 5/02*** (2006.01), ***C08B 11/193*** (2006.01), ***C08F 220/00*** (2006.01), ***C08G 61/02*** (2006.01), ***G03F 7/004*** (2006.01)
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: ***C07C 275/62*** (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
B41C 1/10 (2006.01) , ***B41N 1/14*** (2006.01) , ***C07C 271/08*** (2006.01) , ***C07F 5/02*** (2006.01) , ***C08B 11/193*** (2006.01) ***C08F 220/00*** (2006.01) , ***C08G 61/02*** (2006.01) , ***G03F 7/004*** (2006.01)

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Delphion, Canadian Patent Database, USPTO: iodonium, onium, polymerizable, oligomer, lithographic, infrared, acetal, covalently bonded, urethane, urea, acrylate, methacrylate, vinyl acetate, laser sensitive, CA Plus and STN: structure search and acrylate, methacrylate, vinyl ether, lithograph?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant	Relevant to claim No.
X	CA 1306571 A1 (CHIAO, W B.) 18 August 1992 (18-08-1992) *see page 12 and claims*	1
X	US 4701402 B1 (PATEL, R.C. et al.) 20 October 1987 (20-10-1987) *see column 7 and examples*	1, 17-19, 21-22, 39-42, 58-60 and 63
X	US 6008267 B1 (VALLEE, A. et al.) 28 December 1999 (28-12-1999) *see columns 4-5*	1
X	CA 2299856 AA (OESTREICH, S. et al.) 11 September 2000 (11-09-2000) *see claims*	1
X	US 2002/0015826 A1 (DESMARTEAU, D. et al.) 07 February 2002 (07-02-2002) *see whole document*	1
X	US 2006/0032390 A1 (HOSHI, S. et al.) 16 February 2006 (16-02-2006) *see pages 10-12*	1, 17-19, 21-22, 39-42, 58-60, 63 and 67-75

[X] Further documents are listed in the continuation of Box C.   [X] See patent family 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 application or patent 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	Date of mailing of the international search report
21 August 2007 (21-08-2007)	30 August 2007 (30-08-2007)

Name and mailing address of the ISA/CA
Canadian Intellectual Property Office
Place du Portage I, C114 - 1st Floor, Box PCT
50 Victoria Street
Gatineau, Quebec K1A 0C9
Facsimile No.: 001-819-953-2476

Authorized officer
Karla Randell 819- 956-6118

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2007/000820

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of the first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons :

1. [ ] Claim Nos. :
because they relate to subject matter not required to be searched by this Authority, namely :

2. [ ] Claim Nos. :
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically :

3. [ ] Claim Nos. :
because they are dependant claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III **Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows :

Group 1: Claims 1-75
Group 2: Claims 76-98
Group 3: Claims 99-124

continued on extra sheet, last page

1. [X] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claim Nos. :

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim Nos. :

Remark on Protest [ ] The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

[ ] The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

[ ] No protest accompanied the payment of additional search fees.

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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P, X	EP 1728838 A1 (KUNITA, K. et al.) 06 December 2006 (06-12-2006) *whole document*	1-3, 17-19, 39-42, 58-65 and 67-75
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X Y	EP 1204000 A1 (OSHIMA, Y. et al.) 08 May 2002 (08-05-2002) *whole document*	1, 17-19, 21-22, 39-42, 58-60, 67-75 1-75
Y	US 6548222 B2 (TENG, G.G.) 15 April 2003 (15-04-2003) *whole document*	1-75
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Continuation of Box No. III

Group 1: Claims 1-16 are directed towards an iodonium salt and its preparation. Claims 17-20 are directed towards a coating. Claims 21-75 are directed towards the use of the iodonium salt in a coating comprising acetal coploymers and polymer binders.

Group 2: Claims 76-89 are directed towards an acetal copolymer not containing an iodonium salt. Claims 90-93 are directed towards a coating containing the acetal copolymer. Claims 94-98 are directed towards the use of the acetal coploymer in a coating comprising an iodonium salt and polymer binders.

Group 3: Claims 99-115 are directed towards a polymer binder, not containing an iodonium salt. Claims 116-119 are directed towards a coating containing the polymer binder. Claims 120-124 are directed towards the use of the polymer binder in a coating composition comprising an acetal copolymer and an iodonium salt.