(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
30 December 2015 (30.12.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/200591 A1

(51) International Patent Classification:
C08J 3/28 (2006.01) *B05D 3/02* (2006.01)

(21) International Application Number:
PCT/US2015/037626

(22) International Filing Date:
25 June 2015 (25.06.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/016,877 25 June 2014 (25.06.2014) US

(71) Applicant: **UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC.** [US/US]; 233 Grinter Hall, P.O. Box 115500, Gainesville, FL 32611-5500 (US).

(72) Inventors: **BRENNAN, Anthony, B.**; 3959 NW 37th Place, Gainesville, FL 32606 (US). **VILLADA, Laura, M.**; 204 NW 18th St., Apt. 2, Gainesville, FL 32603 (US). **KIZILKAYA, Canan**; 2601 SW Archer Road, University Commons, Apt. 302, Building A, Gainesville, FL 32608 (US).

(74) Agent: **RODRIGUES, David, E.**; Cantor Colburn LLP, 20 Church Street, 22nd Floor, Hartford, CT 06103 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2015/200591 A1

(54) Title: POLYURETHANES, ARTICLES COMPRISING THE SAME AND METHODS OF MANUFACTURE THEREOF

(57) Abstract: Disclosed herein a composition comprising a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof. Disclosed herein too is a composition comprising a urethane of the Figure 3; where hydroxyl or amine linkages of the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof; and a polymeric resin.

POLYURETHANES, ARTICLES COMPRISING THE SAME AND METHODS OF MANUFACTURE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/016,877 filed on June 25th 2014, the entire contents of which are hereby incorporated by reference in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH & DEVELOPMENT

[0002] This invention was made with government support under Contract Number N000141310443 awarded by the Office of Naval Research. The government has certain rights in the invention.

BACKGROUND

[0003] This disclosure relates to polyurethanes, articles comprising the same and to methods of manufacture thereof. In particular, this disclosure relates to a fluorinated non-isocyanate urethane dimethacrylate resin.

[0004] Polyurethane is a polymer composed of a chain of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available. Polyurethane polymers are traditionally and most commonly formed by reacting a di- or polyisocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule. Some noteworthy recent efforts have been dedicated to minimizing the use of isocyanates to synthesize polyurethanes, because the isocyanates raise severe toxicity issues. Non-isocyanate based polyurethanes (NIPUs) have recently been developed as a new class of polyurethane polymers to mitigate health and environmental concerns.

[0005] To overcome these problems, it is desirable to manufacture polyurethanes via a route that does not involve the use of isocyanates. In addition, it is desirable to functionalize these polyurethanes with functional groups that contain other atoms (e.g., fluorine, silicon, phosphorus, and the like) so as to provide the polyurethane with a range of properties that render the resulting material capable of being used in a variety of applications.

SUMMARY

[0006] Disclosed herein a composition comprising a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof.

[0007] Disclosed herein too is a composition comprising a urethane of the Figure 3; where hydroxyl or amine linkages of the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof; and a polymeric resin.

[0008] Disclosed herein too is an article comprising a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof; and a substrate upon which the fluorinated urethane methacrylate is disposed.

[0009] Disclosed herein too is a method comprising reacting a cyclic carbonate with a diamine to form a urethane; reacting the urethane with a methacrylate to form a non-isocyanate urethane methacrylate; and functionalizing the non-isocyanate urethane methacrylate with a molecule that contains fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof.

[0010] Disclosed herein too is an article comprising a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof.

BRIEF DESCRIPTION OF THE FIGURES

[0011] Figure 1 depicts the reaction between carbon dioxide and an oxirane ring to form cyclic carbonates;

[0012] Figure 2 shows the reaction of a cyclic carbonate with a diamine to form a urethane;

[0013] Figure 3 shows the endcapping of the various non-isocyanate urethanes (from the Figure 2) with 4-methylene-1,3-dioxolane;

[0014] Figure 4 shows the functionalization of the various non-isocyanate urethane methacrylates with 4-methylene-1,3-dioxolane;

[0015] Figure 5 shows the functionalization of the various non-isocyanate urethanes from the Figure 2 with a methacrylate;

[0016] Figures 6 shows the functionalization of the a non-isocyanate urethane dioxolane from the Figure 3 with phosphoric acid;

[0017] Figures 6(A) and 6 (B) show the functionalization of the a fluorinated non-isocyanate urethane dioxolane from the Figure 3 with phosphoric acid;

[0018] Figure 7 shows the functionalization of the a non-isocyanate urethane dioxolane from the Figure 3 with sulfonic acid or an anhydride;

[0019] Figures 7(A) and 7 (B) show the functionalization of a fluorinated non-isocyanate urethane dioxolane with sulfonic acid;

[0020] Figures 7(C) and (D) show the functionalization of a fluorinated non-isocyanate urethane dioxolane with any anhydride;

[0021] Figure 8 shows the reaction of a cyclic carbonate with a cyclic diamine to form a urethane;

[0022] Figure 9 shows the reaction of the urethane with a methacrylate to form a non-isocyanate urethane dimethacrylate;

[0023] Figure 10 shows one exemplary embodiment of how a non-isocyanate urethane dimethacrylate can be used to form a hydrogel;

[0024] Figure 11 shows on exemplary embodiment of the reaction of the non-isocyanate urethane dimethacrylate with a fluorine containing molecule to produce a fluorinated non-isocyanate urethane dimethacrylate;

[0025] Figures 12 – 19(A) show various exemplary structures of non-isocyanate urethanes functionalized with fluorine containing molecules, sulfur containing molecules, phosphorus containing molecules and anhydride functionalized molecules.

DETAILED DESCRIPTION

[0026] Disclosed herein is a non-isocyanate route to synthesizing fluorinated polyurethane methacrylates (hereinafter fluorinated polyurethane methacrylate). In an exemplary embodiment, the fluorinated polyurethane methacrylate can be functionalized with molecules that contain phosphorus atoms, silicon atoms, or other reactive functionalities that render important properties to the resulting molecule. These properties can involve flame retardancy, moisture uptake, abrasion resistance and the like.

[0027] In conventional polyurethane (PU) preparation processes, the polyurethane is synthesized by using isocyanates (such as diisocyanates and polyisocyanates) and polyols (such as diols or polydhydroxy polyols with high functionality) as major raw materials, but the manufacturing process of this sort usually requires phosgene which is a severely toxic pollutant. If the phosgene is leaked accidentally during the manufacturing process, the phosgene will pose an immediate threat to our environment and jeopardize our health such as causing pulmonary edema, and the manufacturing process itself will lead to a certain degree of risk. Therefore, scientists attempt to use non-isocyanates routes (which use absolutely no isocyanates at all) to manufacture polyurethane.

[0028] Polyurethanes can be manufactured by a method that involves not using any diisocyanates, wherein five-membered cyclic carbonates (Bis(cyclic carbonate)s) and primary amines are reacted at room temperature to produce a high yield of β-position hydroxyl polyurethane (2-hydroxyethylurethane), and the reaction is represented by the chemical equations shown in the Figures 1 and 2.

[0029] Figure 1 shows the reaction between carbon dioxide and an oxirane ring to produce cyclic carbonates. Figure 1 depicts the reaction between carbon dioxide and the oxirane ring for both single cyclic carbonates and bicyclic carbonates. As shown in the Figure 1, the cyclic carbonates are manufactured by a nucleophilic ring opening reaction of oxirane and carbon dioxide. The cyclic carbonate is manufactured by the reaction of oxirane with carbon dioxide in the presence of a catalyst. The catalyst can include an amine, a phosphine, a quaternary ammonium salt, an antimony compound, a porphyrin, and/or a transition metal complex. The reaction to produce the cyclic carbonate can be produced at a variety of different pressures ranging from atmospheric pressure to high pressures of 10 to 50 atmospheres. Figure 2 shows the reaction between the cyclic carbonates and diamines to produce the non-isocyanate urethanes. A variety of reactions that result in the production of non-isocyanate urethanes are shown in the Figure 2. As can be seen, the reaction takes place at room temperature in the presence of a solvent such as dichloromethane. The reaction can also take place at elevated temperatures if desired.

[0030] Examples of diamines that may be used in the reaction of Figure 2 are linear aliphatic diamines (e.g., ethylenediamine (1,2-diaminoethane), drerivatives of ethylene diamines such as N-alkylated compounds (ethambutol) and tetramethylethylenediamine, propane-1,3-diamine, butane-1,4-diamine, pentane-1,5-diamine, hexamethylenediamine (hexane-1,6-diamine), or combinations thereof), branched aliphatic diamines (e.g., 1,2-diaminopropane, diphenylethylenediamine, which is C2-symmetric, diaminocyclohexane,

which is C2-symmetric, or combinations thereof), xylylenediamines (e.g., o-xylylenediamine, m-xylylenediamine, p-xylylenediamine, or combinations thereof), aromatic diamines (e.g., phenylenediamines such as o-phenylenediamine or OPD, m-phenylenediamine or MPD, p-phenylenediamine or PPD, 2,5-diaminotoluene is related to PPD but contains a methyl group on the ring, various N-methylated derivatives of the phenylenediamines such as dimethyl-4-phenylenediamine, N,N'-di-2-butyl-1,4-phenylenediamine, 4,4'-diaminobiphenyl, 1,8-diaminonaphthalene, or combinations thereof), cyclic diamines, polyamines or the like, or combinations thereof.

[0031] The reactions shown in the Figures 1 and 2 may be conducted in a variety of different solvents such as liquid carbon dioxide, dimethylformamide, dimethylacetamide, dimethylsulfoxide, and the like. The polyurethanes thus produced may be end functionalized with a variety of different molecules. The R_1 and R_2 moieties on the non-isocyanate urethane molecule are discussed in detail below.

[0032] Figures 3 – 7 show a variety of different reactions that can be conducted with the non-isocyanate urethanes that impart different properties and capabilities to the molecule. The Figures 3 and 4 show the endcapping of the various non-isocyanate urethanes (from the Figure 2) with 4-methylene-1,3-dioxolane.

[0033] The reaction between the 4-methylene-1,3-dioxolane and the non-isocyanate urethane can be conducted in a variety of different solvents. Liquid aprotic polar solvents such as water, propylene carbonate, ethylene carbonate, butyrolactone, acetonitrile, benzonitrile, nitromethane, nitrobenzene, sulfolane, dimethylformamide, N-methylpyrrolidone, or the like, or combinations comprising at least one of the foregoing solvents are generally desirable. Polar protic solvents such as, but not limited to, methanol, acetonitrile, nitromethane, ethanol, propanol, isopropanol, butanol, or the like, or combinations comprising at least one of the foregoing polar protic solvents may be used. Other non-polar solvents such a liquid carbon dioxide, supercritical carbon dioxide, benzene, toluene, methylene chloride, carbon tetrachloride, hexane, diethyl ether, tetrahydrofuran, or the like, or combinations comprising at least one of the foregoing solvents may also be used. Co-solvents comprising at least one aprotic polar solvent and at least one non-polar solvent may also be utilized. Ionic liquids, which mainly comprise the imidazolium salts, may also be utilized for swelling the polymer. An exemplary solvent for conducting the 4-methylene-1,3-dioxolane endcapping reaction is tetrahydrofuran (THF).

[0034] These endcapping reactions (seen in the Figures 3 and 4) can be conducted at temperatures of -30°C to 100°C, and preferably -10°C to 35°C. Reaction pressure may be varied from below atmospheric pressure (i.e., a vacuum) to pressures as high as 100 psi.

[0035] As can be seen in the Figure 3, the 4-methylene-1,3-dioxolane reacts with the amine functionality at the end of the non-isocyanate urethane molecule to endcap the molecule. In the Figure 4, the 4-methylene-1,3-dioxolane molecule is reacted with the hydroxyl functionality on the cyclohexyl ring. In the Figure 4, it may also be seen that the non-isocyanate urethane is methacrylate endcapped prior to being reacted with the 4-methylene-1,3-dioxolane molecule.

[0036] The functionalization of the non-isocyanate urethane with the 4-methylene-1,3-dioxolane provides the non-isocyanate urethane molecule with ring opening capabilities that can be further used to crosslink the molecule. 4-methylene-1,3-dioxolane endcapped polyurethanes can thus be used as dental resins. When used as a dental resin, ring opening polymerization conducted during the crosslinking process results in lower shrinkage when compared with other polyurethanes that are not 4-methylene-1,3-dioxolane end functionalized. In addition, by using the appropriate substituents for the functional group R1 (in the Figure 3), dendritic molecules can be produced.

[0037] The Figures 5 – 7 shows the functionalization of the non-isocyanate urethane with methacrylates, phosphoric acid, sulfonic acid or an anhydride. As noted above, the functionalization can be conducted at the amine functionalized end of the non-isocyanate urethane molecule or at the hydroxyl moiety on the cyclohexyl molecule. While the Figures 5 – 7 show that the hydroxyl moiety is at the para-position with regard to the bridging moiety R_1, it is envisioned that the hydroxyl moiety can be located at the ortho or meta positions and can be reacted with other functional molecules such as, for example, those shown in the Figures 5 – 7. It is to be noted that the Figure 5 depicts the end functionalization of the non-isocyanate urethane with a methacrylate functionality prior to functionalization with the 4-methylene-1,3-dioxolane molecule. Figure 6(A) shows the functionalization of the a fluorinated non-isocyanate urethane dioxolane from the Figure 3 with phosphoric acid; Figures 7(A) and 7 (B) show the functionalization of a fluorinated non-isocyanate urethane dioxolane with sulfonic acid; and the Figures 7(C) and 7(D) show the functionalization of a fluorinated non-isocyanate urethane dioxolane with any anhydride.

[0038] In one embodiment, the non-isocyanate urethane can be functionalized with unsaturated carboxylic acids are maleic acid, fumaric acid, itaconic add, acrylic acid, methacrylic acid, crotonic acid, and citraconic acid. Examples of derivatives of unsaturated

carboxylic acids are maleic anhydride, citraconic anhydride, itaconic anhydride, methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate, butyl methacrylate, glycidyl acrylate, glycidyl methacrylate, or the like, or a combination thereof. Maleic anhydride is the preferred grafting compound for functionalizing the non-isocyanate urethanes.

[0039] In one exemplary embodiment, the non-isocyanate urethane can be functionalized with molecules that have fluorine atoms to provide the polyurethanes with unique functional properties. These polyurethanes are called fluorinated non-isocyanate urethane dimethacrylate resins and can be used in a variety of different applications. The manufacturing of these fluorinated non-isocyanate urethane dimethacrylate resins is detailed in the Figures 8 – 10.

[0040] In the Figure 8, the cyclic carbonate is reacted with a cyclic isophorondiamine to produce an asymmetric non-isocyanate urethane that is endcapped with the cyclic diamine. The Figure 8 depicts one method of endcapping the cyclic carbonate with a cyclic diamine. The cyclic diamine is 5-amino-1,3,3-trimethylcyclohexanemethylamine (IPDA).

[0041] The reaction is conducted in the presence of a dichloromethane solvent and the reactants are covered in a blanket of nitrogen during the reaction. About 0.5 to 2.3 moles of the diamine are used per mole of the cyclic carbonate. The reaction temperature is 0 to 70°C, preferably 20 to 30C° and the reaction pressure is 0.1 atmosphere to 20 atmospheres, preferably 1 to 2 atmospheres. The reaction may be conducted in a batch or in a continuous reactor, preferably in a batch reactor. It is to be noted that other solvents listed above may also be used in lieu of or in conjunction with the dichloromethane.

[0042] The non-isocyanate urethane functionalized with the cyclic isophorondiamine of the Figure 8 is then reacted with a methacrylate (3-acryloyloxy -2- hydroxypropyl methacrylate (AHM)) in the presence of dichloromethane under a blanket of nitrogen as shown in the Figure 9 to form a dimethacrylate functionalized urethane. With reference to the Figure 9, about 1.9 to 2.3 moles of the dimethacrylate are used per mole of the non-isocyanate urethane. The reaction temperature is -10 to 70°C, preferably 20 to 30°C and the reaction pressure is 0.1 atmosphere to 20 atmospheres, preferably 1 to 2 atmospheres. The reaction may be conducted in a batch or in a continuous reactor, preferably in a batch reactor. In an embodiment, the reaction of the Figure 9 can be conducted in the same reactor as that of the Figure 8. The reaction of the Figure 8 is detailed in U.S. Patent Publication No. 20130004467 to Jing-Zhong Hwang et al., the entire contents of which are hereby incorporated by reference.

[0043] The dimethacrylate functionalized urethane of the Figure 9 can be cured using radiation or can be cured thermally to create a hydrogel. Radiation includes ultraviolet radiation, microwave radiation, xray radiation, electron beam radiation and the like. The Figure 10 shows how the dimethacrylate functionalized urethane of the Figure 9 (optionally containing a polydimethylsiloxane molecule) may be mixed with other methacrylates such as hydroxyethylmethacrylate (HEMA) and hexafluorobutyl methacrylate (HFMA) to form a mixture. The mixture can then be applied to a surface and then irradiated to form a hydrogel. By varying the ratio of HFMA to HEMA and the dimethacrylate functionalized urethane, the hydrophobicity of the surface can be controlled. In addition, by varying the amount of the optional polysiloxane in the dimethacrylate functionalized urethane, the hydrophobicity of the surface can also be controlled.

[0044] In a hydrogel formulation, the HEMA is present in an amount of 50 to 90 mole percent, preferably 60 to 80 mole percent, based upon the total number of moles of the composition. The HFMA is present in an amount of 5 to 30 mole percent, preferably 10 to 20 mole percent, based upon the total number of moles of the composition. The dimethacrylate functionalized urethane is present in an amount of 5 to 20, preferably 6 to 15 mole percent based upon the total number of moles of the hydrogel composition. The hydrogel composition may use a catalyst, an initiator and/or a curing agent as desired.

[0045] In one embodiment, the dimethacrylate functionalized urethane can be functionalized with a fluorine containing molecule to form the fluorinated non-isocyanate urethane methacrylate. The Figure 11 depicts the functionalization of the dimethacrylate functionalized urethane to form the fluorinated non-isocyanate urethane methacrylate. The reaction of the Figure 11 is conducted in the presence of dichloromethane under a blanket of nitrogen. With reference to the Figure 11, about 0.1 to 7.2 moles of the fluorine containing molecule are used per mole of the dimethacrylate functionalized urethane. In one embodiment, the fluorine containing molecule is perfluorobutyryl chloride. The reaction temperature is -10 to 70°C, preferably -5 to 10°C and the reaction pressure is 0.1 atmosphere to 20 atmospheres, preferably 1 to 2 atmospheres. The reaction may be conducted in a batch or in a continuous reactor, preferably in a batch reactor. In an embodiment, the reaction of the Figure 11 can be conducted in the same reactor as that of the Figure 9.

[0046] With regard to the Figure 11, it may be seen that that the fluorine containing molecule can react with the dimethacrylate functionalized urethane at either the hydroxyl moiety or at the amine moiety. In one embodiment, some of the hydroxyl moieties (on the dimethacrylate functionalized urethane) can be reacted with the fluorine containing molecules

with other can be reacted with molecules that contain phosphorus, silicon, sulfur, boron, and the like. Some of these alternative functionalization schemes are shown in the Figures 5 – 7. In another embodiment, some of the amine moieties (on the dimethacrylate functionalized urethane) can be reacted with the fluorine containing molecules with other can be reacted with molecules that contain phosphorus, silicon, sulfur, and the like. Some of these alternative functionalization schemes are shown in the Figures 5 – 7 above.

[0047] The fluorinated non-isocyanate urethane methacrylate can be used in a variety of different applications. In one embodiment depicted in the Figure 11, it can be used to coat surfaces and to control the hydrophobicity of the surface.

[0048] With reference now once again to the Figures 1 - 3, it may be seen that the bridging moieties R_1 and R_2 can be selected from a variety of different organic molecules. The bridging moieties R_1 and R_2 can be selected from a variety of different organic groups that are shown below.

[0049] R_1 and/or R_2 in the Figures 1 - 3 may be an aromatic organic group, for example, a group of the formula (1):

$$-\!\!-\!\!-A^1-\!\!-Y^1-\!\!-A^2-\!\!-\!\!-\!\!- \qquad (1)$$

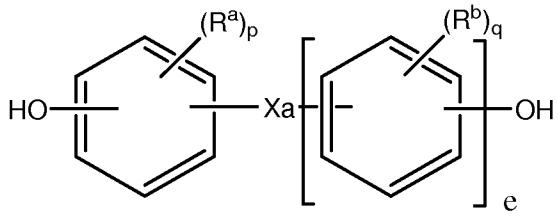
wherein each of the A^1 and A^2 is an alkyl group, a cycloalkyl group or a monocyclic divalent aryl group and Y^1 is a bridging group that separates A^1 and A^2. In one embodiment, Y^1 can comprise one or two atoms. For example, one atom may separate A^1 from A^2, with illustrative examples of these groups including –O-, -S-, -S(O)-, -$S(O)_2$)-, -C(O)-, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecyclidene, cyclododecylidene, and adamantylidene. The bridging group of Y^1 may be a hydrocarbon group or a saturated hydrocarbon group such as methylene, cyclohexlylidene, or isopropylidene.

[0050] In another embodiment, the bridging group Y^1 may contain 3 or more atoms. Examples of bridging groups that contain 3 or more atoms are C_2 to C_{18} alkyl groups, C_3 to C_{18} cycloalkyl groups, fused aryl groups, polymeric molecules and the like. Further details are provided below.

[0051] In one embodiment, R_1 may be derived from dihydroxy compounds having the formula HO-R_1-OH, wherein R_1 is defined as above for formula (1). The formula HO-R_1-OH includes bisphenol compounds of the formula (2):

$$HO-\!\!-A^1-\!\!-Y^1-\!\!-A^2-\!\!-OH \qquad (2)$$

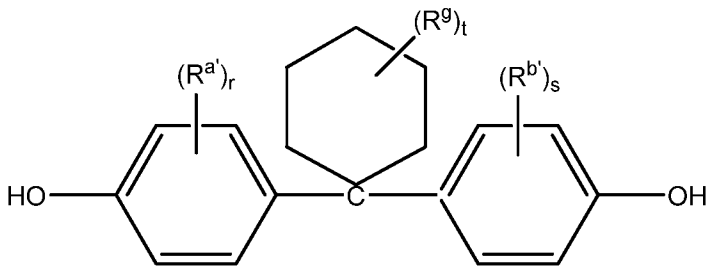
wherein Y^1, A^1, and A^2 are as described above. For example, one atom may separate A^1 and A^2. Each R_1 may include bisphenol compounds of the general formula (3):



(3)

where X_a is a bridging group connecting the two hydroxy-substituted aromatic groups, where the bridging group and the hydroxy substituent of each C_6 arylene group are disposed ortho, meta, or para (specifically para) to each other on the C_6 arylene group. For example, the bridging group X_a may be single bond, --O--, --S--, --C(O)--, or a C_{1-18} organic group. The C_{1-18} organic bridging group may be cyclic or acyclic, aromatic or non-aromatic, and can further comprise heteroatoms such as halogens, oxygen, nitrogen, sulfur, silicon, or phosphorous. The C_{1-18} organic group can be disposed such that the C_6 arylene groups connected thereto are each connected to a common alkylidene carbon or to different carbons of the C_{1-18} organic bridging group. R^a and R^b may each represent a halogen, C_{1-12} alkyl group, or a combination thereof. For example, R^a and R^b may each be a C_{1-3} alkyl group, specifically methyl, disposed meta to the hydroxy group on each arylene group. The designation (e) is 0 or 1. The numbers p and q are each independently integers of 0 to 4. It will be understood that R^a is hydrogen when p is 0, and likewise R^b is hydrogen when q is 0.

[0052] X_a may be substituted or unsubstituted C_{3-18} cycloalkylidene, a C_{1-25} alkylidene of formula --$C(R^c)(R^d)$-- wherein R^c and R^d are each independently hydrogen, C_{1-12} alkyl, C_{1-12} cycloalkyl, C_{7-12} arylalkyl, C_{1-12} heteroalkyl, or cyclic C_{7-12} heteroarylalkyl, or a group of the formula --$C(=R^e)$-- wherein R^e is a divalent C_{1-12} hydrocarbon group. This may include methylene, cyclohexylmethylene, ethylidene, neopentylidene, isopropylidene, 2-[2.2.1]-bicycloheptylidene, cyclohexylidene, cyclopentylidene, cyclododecylidene, and adamantylidene. A specific example wherein X_a is a substituted cycloalkylidene is the cyclohexylidene-bridged, alkyl-substituted bisphenol of formula (4):

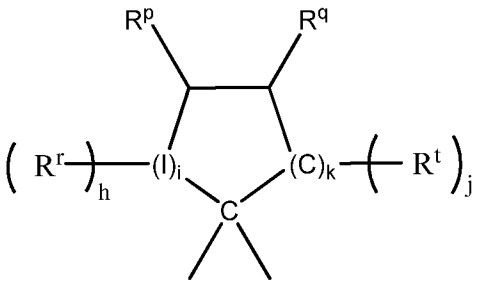


(4)

wherein $R^{a'}$ and $R^{b'}$ are each independently C_{1-12} alkyl, R^g is C_{1-12} alkyl or halogen, r and s are each independently 1 to 4, and t is 0 to 10. $R^{a'}$ and $R^{b'}$ may be disposed meta to the cyclohexylidene bridging group. The substituents $R^{a'}$, $R^{b'}$ and R^g may, when comprising an appropriate number of carbon atoms, be straight chain, cyclic, bicyclic, branched, saturated, or unsaturated. For example, R^g may be each independently C_{1-4} alkyl, R^g is C_{1-4} alkyl, r and s are each 1, and t is 0 to 5. In another example, $R^{a'}$, $R^{b'}$ and R^g may each be methyl, r and s are each 1, and t is 0 or 3. The cyclohexylidene-bridged bisphenol can be the reaction product of two moles of o-cresol with one mole of cyclohexanone. In another example, the cyclohexylidene-bridged bisphenol may be the reaction product of two moles of a cresol with one mole of a hydrogenated isophorone (e.g., 1,1,3-trimethyl-3-cyclohexane-5-one). Such cyclohexane-containing bisphenols, for example the reaction product of two moles of a phenol with one mole of a hydrogenated isophorone, are useful for making polycarbonate polymers with high glass transition temperatures and high heat distortion temperatures. Cyclohexyl bisphenol-containing polycarbonates, or a combination comprising at least one of the foregoing with other bisphenol polycarbonates, are supplied by Bayer Co. under the APEC® trade name.

[0053] In one embodiment, X_a is a C_{1-18} alkylene group, a C_{3-18} cycloalkylene group, a fused C_{6-18} cycloalkylene group, or a group of the formula --B_1—W—B_2-- wherein B_1 and B_2 are the same or different C_{1-6}alkylene group and W is a C_{3-12} cycloalkylidene group or a C_{6-16} arylene group.

[0054] In another example, X_a may be a substituted C_{3-18} cycloalkylidene of the formula (5):

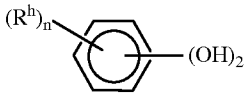


(5)

wherein R^r, R^p, R^q, and R^t are independently hydrogen, halogen, oxygen, or C_{1-12} organic groups; I is a direct bond, a carbon, or a divalent oxygen, sulfur, or -N(Z)- where Z is hydrogen, halogen, hydroxy, C_{1-12} alkyl, C_{1-12} alkoxy, C_{6-12} aryl, or C_{1-12} acyl; h is 0 to 2, j is 1 or 2, i is an integer of 0 or 1, and k is an integer of 0 to 3, with the proviso that at least two of R^r, R^p, R^q and R^t taken together are a fused cycloaliphatic, aromatic, or heteroaromatic ring. It will be understood that where the fused ring is aromatic, the ring as shown in formula

(5) will have an unsaturated carbon-carbon linkage at the junction where the ring is fused. When i is 0, h is 0, and k is 1, the ring as shown in formula (5) contains 4 carbon atoms; when i is 0, h is 0, and k is 2, the ring as shown contains 5 carbon atoms, and when i is 0, h is 0, and k is 3, the ring contains 6 carbon atoms. In one example, two adjacent groups (e.g., R^q and R^t taken together) form an aromatic group, and in another embodiment, R^q and R^t taken together form one aromatic group and R^r and R^p taken together form a second aromatic group. When R^q and R^t taken together form an aromatic group, R^p can be a double-bonded oxygen atom, *i.e.*, a ketone.

[0055] Other useful dihydroxy compounds having the formula HO-R_1-OH include aromatic dihydroxy compounds of formula (6):



(6)

wherein each R^h is independently a halogen atom, a C_{1-10} hydrocarbyl such as a C_{1-10} alkyl group, a halogen substituted C_{1-10} hydrocarbyl such as a halogen-substituted C_{1-10} alkyl group, and n is 0 to 4. The halogen is usually bromine.

[0056] Bisphenol-type dihydroxy aromatic compounds may include the following: 4,4'-dihydroxybiphenyl, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)diphenylmethane, bis(4-hydroxyphenyl)-1-naphthylmethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 2-(4-hydroxyphenyl)-2-(3-hydroxyphenyl)propane, bis(4-hydroxyphenyl)phenylmethane, 2,2-bis(4-hydroxy-3-bromophenyl)propane, 1,1-bis(hydroxyphenyl)cyclopentane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxy-3 methyl phenyl)cyclohexane 1,1-bis(4-hydroxyphenyl)isobutene, 1,1-bis(4-hydroxyphenyl)cyclododecane, trans-2,3-bis(4-hydroxyphenyl)-2-butene, 2,2-bis(4-hydroxyphenyl)adamantine, (alpha, alpha'-bis(4-hydroxyphenyl)toluene, bis(4-hydroxyphenyl)acetonitrile, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-ethyl-4-hydroxyphenyl)propane, 2,2-bis(3-n-propyl-4-hydroxyphenyl)propane, 2,2-bis(3-isopropyl-4-hydroxyphenyl)propane, 2,2-bis(3-sec-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-t-butyl-4-hydroxyphenyl)propane, 2,2-bis(3-cyclohexyl-4-hydroxyphenyl)propane, 2,2-bis(3-allyl-4-hydroxyphenyl)propane, 2,2-bis(3-methoxy-4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dibromo-2,2-bis(4-hydroxyphenyl)ethylene, 1,1-dichloro-2,2-bis(5-phenoxy-4-hydroxyphenyl)ethylene, 4,4'-dihydroxybenzophenone, 3,3-bis(4-hydroxyphenyl)-2-

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

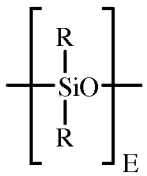
[0057] Examples of the types of bisphenol compounds represented by formula (2) may include 1,1-bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane (hereinafter "bisphenol A" or "BPA"), 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)octane, 1,1-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)n-butane, 2,2-bis(4-hydroxy-1-methylphenyl)propane, 1,1-bis(4-hydroxy-t-butylphenyl)propane, 3,3-bis(4-hydroxyphenyl)phthalimidine, 2-phenyl-3,3-bis(4-hydroxyphenyl)phthalimidine ("PBPP"), 9,9-bis(4-hydroxyphenyl)fluorene, and 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane ("DMBPC"). Exemplary polymers and copolymers (that are used in the R_1 position) containing polycarbonate units may be derived from bisphenol A.

[0058] As detailed above, R_1can be a polymer. In one embodiment, R_1 is a polyolefin, a polycarbonate, a polyalkylene glycol, a polyester-carbonate, a polysiloxane, a polycarbonate-siloxane, a poly(meth)acrylate, a poly(meth)acrylate-siloxane, a polyalkyl(meth)acrylate, a polyalkyl(meth)acrylate-siloxane, a polyetherketone, a polysulfone, a polyphosphazene, a polyphosphonate, a polyimide, a polyetherimide, a polyacetal, a polyacrylic, a polystyrene, a polyester, a polyamide, a polyamideimide, a polyarylate, a polyarylsulfone, a polyethersulfone, a polyphenylene sulfide, a polyvinyl chloride, a polyfluoroethylene, a polyether etherketone, a polyether ketone ketone, a polybenzoxazole, a polyoxadiazole, a polybenzothiazinophenothiazine, a polybenzothiazole, a polypyrazinoquinoxaline, a polypyromellitimide, a polyquinoxaline, a polybenzimidazole, a polyoxindole, a polyoxoisoindoline, a polydioxoisoindoline, a polytriazine, a polypyridazine, a polypiperazine, a polypyridine, a polypiperidine, a polytriazole, a polypyrazole, a polypyrrolidine, a polycarborane, a polyoxabicyclononane, a polydibenzofuran, a polyphthalide, a polyanhydride, a polyvinyl ether, a polyvinyl thioether, a polyvinyl alcohol, a polyvinyl ketone, a polyvinyl halide, a polyvinyl nitrile, a polyvinyl ester, a polysulfonate, a

polysulfide, a polythioester, a polysulfonamide, a polyurea, a polyphosphazene, a polysilazane, or the like, or a combination thereof.

[0059] Resorbable or biodegradable polymers may also be used. These include polylactic-glycolic acid (PLGA), poly-caprolactone (PCL), copolymers of polylactic-glycolic acid and poly-caprolactone (PCL-PLGA copolymer), polyhydroxy-butyrate-valerate (PHBV), polyorthoester (POE), polyethylene oxide-butylene terephthalate (PEO-PBTP), poly-D,L-lactic acid-p-dioxanone-polyethylene glycol block copolymer (PLA-DX-PEG), or the like, or a combination thereof.

[0060] In one embodiment, R_1 or R_2 is preferably a polycarbonate, a polysiloxane, a polyester carbonate, a polycarbonate-siloxane or a polyester-siloxane. In an embodiment, the polysiloxane is represented by the formula (7):

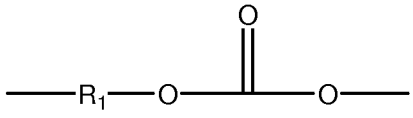


(7)

wherein each R is independently a C_{1-13} monovalent organic group. For example, R can be a C_1-C_{13} alkyl, C_1-C_{13} alkoxy, C_2-C_{13} alkenyl group, C_2-C_{13} alkenyloxy, C_3-C_6 cycloalkyl, C_3-C_6 cycloalkoxy, C_6-C_{14} aryl, C_6-C_{10} aryloxy, C_7-C_{13} arylalkyl, C_7-C_{13} aralkoxy, C_7-C_{13} alkylaryl, or C_7-C_{13} alkylaryloxy. Combinations of the foregoing R groups can be used in the same copolymer.

[0061] The value of E in formula (7) can vary widely depending on the type and relative amount of each component in the flame retardant composition, the desired properties of the composition, and like considerations. Generally, E has an average value of 2 to 1,000, specifically 3 to 500, more specifically 5 to 100. Polysiloxane-carbonate copolymers may also be used in the R_1 or R_2 positions.

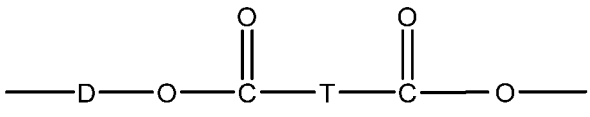
[0062] As noted above, R_1 or R_2 may be a polyestercarbonate, also known as a polyester-polycarbonate. The polycarbonate portion may be defined as follows in the formula (8:



(8)

where R_1 is the dihydroxy compound as defined above in the formulas (1), (2) or (6) and wherein at least 60 percent of the total number of R^1 groups may contain aromatic organic groups and the balance thereof are aliphatic or alicyclic, or aromatic groups.

[0063] In another embodiment, R_1 and/or R_2 is a polyester carbonate as shown in the formula (9)



(9)

wherein O-D-O is a divalent group derived from a dihydroxy compound, and D may be, for example, one or more alkyl containing C_6-C_{20} aromatic group(s), or one or more C_6-C_{20} aromatic group(s), a C_{2-10} alkylene group, a C_{6-20} alicyclic group, a C_{6-20} aromatic group or a polyoxyalkylene group in which the alkylene groups contain 2 to 6 carbon atoms, specifically 2, 3, or 4 carbon atoms. D may be a C_{2-30} alkylene group having a straight chain, branched chain, or cyclic (including polycyclic) structure. O-D-O may be derived from the formulas (1), (2) and (6) above. T of formula (8) may be a divalent group derived from a dicarboxylic acid, and may be, for example, a C_{2-10} alkylene group, a C_{6-20} alicyclic group, a C_{6-20} alkyl aromatic group, a C_{6-20} aromatic group, or a C_6 to C_{36} divalent organic group derived from a dihydroxy compound or chemical equivalent thereof. In an embodiment, T is an aliphatic group. T may be derived from a C_6-C_{20} linear aliphatic alpha-omega (α-Ω) dicarboxylic ester. Diacids from which the T group in the ester unit of formula (8) is derived include aliphatic dicarboxylic acid from 6 to 36 carbon atoms, optionally from 6 to 20 carbon atoms. The C_6-C_{20} linear aliphatic alpha-omega (αΩ) dicarboxylic esters may be derived from adipic acid, sebacic acid, 3,3-dimethyl adipic acid, 3,3,6-trimethyl sebacic acid, 3,3,5,5-tetramethyl sebacic acid, azelaic acid, dodecanedioic acid, dimer acids, cyclohexane dicarboxylic acids, dimethyl cyclohexane dicarboxylic acid, norbornane dicarboxylic acids, adamantane dicarboxylic acids, cyclohexene dicarboxylic acids, C_{14}, C_{18} and C_{20} diacids.

[0064] While the Figures 1 – 3 do not reflect a fluorinated non-isocyanate urethane dimethacrylate resin, it can be envisioned that the methacrylate functionalized urethanes of the Figure 3 can be fluorinated as detailed in the Figure 10 while at the same time having R_1 and R_2 selected from amongst the foregoing functional groups. In an exemplary embodiment, the bridging moiety R_1 and/or R_2 is a polysiloxane.

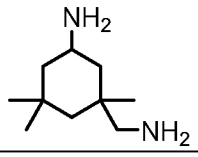
[0065] Figures 12 – 19 show various exemplary structures of non-isocyanate acrylates functionalized with fluorine containing molecules, sulfur containing molecules, phosphorus containing molecules and anhydride functionalized molecules.

[0066] The fluorinated non-isocyanate urethane dimethacrylate resin may be used to manufacture a variety of different articles. In one embodiment, the fluorinated non-

isocyanate urethane dimethacrylate resin may be used as a coating to control the hydrophobicity/hydrophilicity of surfaces. In another embodiment, the fluorinated non-isocyanate urethane dimethacrylate resin may be partially functionalized with phosphoric acid to impart flame retardancy to other compositions that contain it. In yet another embodiment, the urethane functionalized methacrylate (without the fluorine) can be partially or fully functionalized with phosphoric acid to impart flame retardancy to other compositions that contain it. Such a flame retardant composition could be made so as to be devoid of halogens. The use of polysiloxanes as R_1 and/or R_2 may be used for the production of non-stick article surfaces fi desired.

[0067] Figures 1 – 19A show various structures labelled 1, 2, 3, and so on till structure 50 in the Figure 19A. These structures have various groups labelled R_1, R_2, R, and so on till R_{41} in the Figure 18. Preferred molecules for each of the structures R_1, R_2, R, and so on till R_{41} are shown in the Table 1 below.

Table 1

Figure	Designation	Preferred	Chemical Name
1			
	R_1	CH_3	Methyl
	R_2	CH_2	Methylene
2			
	R_3		5-amino-1,3,3-trimethyl(cyclohexane methylamine)
5			
	R_4	CH_2	Methylene
	R_5	CH_2	Methylene
6			
	R_6	$(CH_2)_4$	Butylene
6A			
	R_7	$(CH_2)_4$	Butylene
	R_8	$(CH_2)_4$	Butylene
	R_9	CF2-CF2	Tetrafluoroethylene
	R_{10}	CF2-CF2	Tetrafluoroethylene
	R_{11}	CF2-CF2	Tetrafluoroethylene
7			
	R_{12}	$(CH_2)_3$	Propylene
	R_{13}	CH_2	Methylene
7A			
	R_{14}	$(CH_2)_4$	Butylene
	R_{15}	$(CH_2)_4$	Butylene
7C			
	R_{16}	CH_2	Methylene
	R_{17}	CH_2	Methylene

11			
	R_{18}	CF_2-CF_2	Tetrafluoroethylene
	R_{19}	CF_2-CF_2	Tetrafluoroethylene
	R_{20}	CF_2-CF_2	Tetrafluoroethylene
13			
	R_{21}	$(CH_2)_4$	Butylene
	R_{22}	$(CH_2)_4$	Butylene
	R_{23}	$(CH_2)_4$	Butylene
14			
	R_{24}	CH_2	Methylene
	R_{25}	CH_2	Methylene
	R_{26}	CH_2	Methylene
15			
	R_{27}	$(CH_2)_4$	Butylene
	R_{28}	$(CH_2)_4$	Butylene
	R_{29}	$(CH_2)_4$	Butylene
16			
	R_{30}	CH_2	Methylene
	R_{31}	CH_2	Methylene
16A			
	R_{32}	CH_2	Methylene
	R_{33}	CH_2	Methylene
17			
	R_{34}	CH_2	Methylene
	R_{35}	CH_2	Methylene
18			
	R_{36}	CF_2-CF_2	Tetrafluoroethylene
	R_{37}	CF_2-CF_2	Tetrafluoroethylene
	R_{38}	CF_2-CF_2	Tetrafluoroethylene
	R_{39}	CF_2-CF_2	Tetrafluoroethylene
	R_{40}	CF_2-CF_2	Tetrafluoroethylene
	R_{41}	CF_2-CF_2	Tetrafluoroethylene

As stated above, Figures 1 – 19A show various structures labelled 1, 2, 3, and so on till structure 50 in the Figure 19A. The names of these structures are provided in the parenthesis in the Table 2 below when they contain the preferred entity shown in the Table 1. For example, when the compound (1) of the Figure 1 has R1 as being a methylene group then its name is given in the parenthesis as 3-methyl-7-oxabicycloheptane. The preferred structure for conducting the reaction involving compound (1) in the Figure 1 is therefore 3-methyl-7-oxabicycloheptane. All Figures 1 – 19A are to be viewed in this manner for preferred substituents (as shown Table 1) and preferred molecules shown in parenthesis in the Table 2 below.

Table 2

Figure	Compound	Chemical Name (preferred molecule)
1		
	1	R_1-Cyclohexyl Epoxide (3-methyl-7-oxabicycloheptane)
	2	R_1-Cyclohexyl Anhydride (5-methylhexahydrobenzo[d][1,3]dioxol-2-one)
	3	R_1-Dicyclohexyl epoxide (di(7-oxabicycloheptan-3-yl)methane)
	4	R_1-Dicyclohexyl Dianhydride (5,5'-methylenebis(hexahydrobenzo[d][1,3]dioxol-2-one))
	5	R_1-Epoxide (2-methyloxirane)
	6	R_1-Anhydride (4-methyl-1,3-dioxolan-2-one)
	7	R_1-Diepoxide (di(oxiran-2-yl)methane)
	8	R_1-Dianhydride (4,4'-methylenebis(1,3-dioxolan-2-one))
2		
	2	R_1-Cyclohexyl Anhydride (5-methylhexahydrobenzo[d][1,3]dioxol-2-one)
	9	Amino, 1,3,-trimethyl(cyclohexyl) methylene urethane (2-hydroxy-4-methylcyclohexyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	4	R_1-Dianhydride (5,5'-methylenebis(hexahydrobenzo[d][1,3]dioxol-2-one))
	10	Diamino urethane (methylenebis(6-hydroxycyclohexane-3,1-diyl) bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	6	R_1-Anhydride (4-methyl-1,3-dioxolan-2-one)
	11a	Isomers of Amino urethane alcohols (3-hydroxy-2-methylpropyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	11b	Isomers of Amino urethane alcohols (2-hydroxypropyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	8	R_1-Dianhydride (4,4'-methylenebis(1,3-dioxolan-2-one))
	12a	Diamino urethane isomer (2,4-dihydroxypentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	12b	Diamino urethane isomer (2,4-bis(hydroxymethyl)pentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))

Table 2 (contd)

Figure	Compound	Chemical Name
2	Cont'd	
	12c	Diamino urethane isomer (2-hydroxy-4-(hydroxymethyl)pentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
3		
	9	Amino, 1,3,-trimethyl(cyclohexyl) methylene urethane ((2-hydroxy-

		4-methylcyclohexyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	13	Diamino urethane cyclamate cyclohexyl alcohol (2-hydroxy-4-methylcyclohexyl (3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
	10	Diamino urethane (methylenebis(6-hydroxycyclohexane-3,1-diyl) bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	14	methylenebis(6-hydroxycyclohexane-3,1-diyl) bis((3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
	11a	Isomers of Amino urethane alcohols (3-hydroxy-2-methylpropyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	15a	3-hydroxy-2-methylpropyl (3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate
	11b	Isomers of Amino urethane alcohols (2-hydroxypropyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	15b	2-hydroxypropyl (3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate
	12a	Diamino urethane isomer (2,4-dihydroxypentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	16a	2,4-dihydroxypentane-1,5-diyl bis((3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
	12b	Diamino urethane isomer (2,4-bis(hydroxymethyl)pentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	16b	2,4-bis(hydroxymethyl)pentane-1,5-diyl bis((3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
	12c	Diamino urethane isomer (2-hydroxy-4-(hydroxymethyl)pentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	16c	2-hydroxy-4-(hydroxymethyl)pentane-1,5-diyl bis((3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
4		
	9	Amino, 1,3,-trimethyl(cyclohexyl) methylene urethane ((2-hydroxy-4-methylcyclohexyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	17	2-hydroxy-4-methylcyclohexyl ((5-((methacryloyloxy)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamate
	10	Diamino urethane (methylenebis(6-hydroxycyclohexane-3,1-diyl) bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	18	methylenebis(6-hydroxycyclohexane-3,1-diyl) bis(((5-((methacryloyloxy)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamate)
	11a	Isomers of Amino urethane alcohols (3-hydroxy-2-methylpropyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	19a	3-hydroxy-2-methylpropyl (2-(5-((methacryloyloxy)amino)-1,3,3-

		trimethylcyclohexyl)ethyl)carbamate
	11b	Isomers of Amino urethane alcohols (2-hydroxypropyl (3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate)
	19b	2-hydroxypropyl (3-(((methacryloyloxy)amino)methyl)-3,5,5-trimethylcyclohexyl)carbamate
	12a	Diamino urethane isomer (2,4-dihydroxypentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	20a	2,4-dihydroxypentane-1,5-diyl bis(((1,3,3-trimethyl-5-((3-methyl-2-methylenebut-3-en-1-yl)amino)cyclohexyl)methyl)carbamate)
	12b	Diamino urethane isomer (2,4-bis(hydroxymethyl)pentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	20b	2,4-bis(hydroxymethyl)pentane-1,5-diyl bis(((1,3,3-trimethyl-5-((3-methyl-2-methylenebut-3-en-1-yl)amino)cyclohexyl)methyl)carbamate)
	12c	Diamino urethane isomer (2-hydroxy-4-(hydroxymethyl)pentane-1,5-diyl bis((3-(aminomethyl)-3,5,5-trimethylcyclohexyl)carbamate))
	20c	2-hydroxy-4-(hydroxymethyl)pentane-1,5-diyl bis(((1,3,3-trimethyl-5-((3-methyl-2-methylenebut-3-en-1-yl)amino)cyclohexyl)methyl)carbamate)
5		
	18	methylenebis(6-hydroxycyclohexane-3,1-diyl) bis(((5-((methacryloyloxy)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamate)
	21	methylenebis(6-((4-methylene-1,3-dioxolan-2-yl)methoxy)cyclohexane-3,1-diyl) bis(((5-((methacryloyloxy)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamate)
6		
	13	Diamino urethane cyclamate cyclohexyl alcohol (2-hydroxy-4-methylcyclohexyl (3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
	22	2-(4-(diethoxyphosphoryl)butoxy)-4-methylcyclohexyl ((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamate
	23	(4-((2-((((3,3-dimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamoyl)oxy)-5-methylcyclohexyl)oxy)butyl)phosphonic acid
6A		
	24	(4-((1-((3-((3-((((5-(N-(3-(3-(acryloyloxy)-2-((2,2,3,3,4,4,4-heptafluorobutanoyl)oxy)propoxy)-3-oxopropyl)-2,2,3,3,4,4,4-heptafluorobutanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-(4-phosphonobutoxy)propoxy)methyl)cyclohexyl)methoxy)-3-((((5-(N-(3-(3-(acryloyloxy)-2-(4-phosphonobutoxy)propoxy)-3-oxopropyl)-2,2,3,3,4,4,4-heptafluorobutanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propan-2-

		yl)oxy)butyl)phosphonic acid
6B		
	25	(4-(2-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-3-((3-((3-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-(4-phosphonobutoxy)propoxy)methyl)cyclohexyl)methoxy)propoxy)butyl)phosphonic acid
7		
	13	Diamino urethane cyclamate cyclohexyl alcohol (2-hydroxy-4-methylcyclohexyl (3,3,5-trimethyl-5-((((4-methylene-1,3-dioxolan-2-yl)methyl)amino)methyl)cyclohexyl)carbamate)
	26	2-(4-(hydroxydimethylene-l6-sulfanyl)butoxy)-4-methylcyclohexyl ((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamate
	27	5-methyl-2-((((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamoyl)oxy)cyclohexyl 2-(2,5-dioxotetrahydrofuran-3-yl)acetate
7A		
	28	4-((1-((3-((3-((((5-(N-(3-(3-(acryloyloxy)-2-((2,2,3,3,4,4,4-heptafluorobutanoyl)oxy)propoxy)-3-oxopropyl)-2,2,3,3,4,4,4-heptafluorobutanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-(4-sulfobutoxy)propoxy)methyl)cyclohexyl)methoxy)-3-((((5-(N-(3-(3-(acryloyloxy)-2-(4-sulfobutoxy)propoxy)-3-oxopropyl)-2,2,3,3,4,4,4-heptafluorobutanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propan-2-yl)oxy)butane-1-sulfonic acid
7B		
	29	4-((1-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-3-((3-((2-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-3-(4-sulfobutoxy)propoxy)methyl)cyclohexyl)methoxy)propan-2-yl)oxy)butane-1-sulfonic acid
7C		
	30	3-((3-((2-(2-(2,5-dioxotetrahydrofuran-3-yl)acetoxy)-3-((((5-(N-(3-(2-(2-(2,5-dioxotetrahydrofuran-3-yl)acetoxy)-3-(methacryloyloxy)propoxy)-3-oxopropyl)-2,2,3,3,4,4,4-heptafluorobutanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)-2-((((5-(N-(3-(2-(2-(2,5-dioxotetrahydrofuran-3-yl)acetoxy)-3-(methacryloyloxy)propoxy)-3-oxopropyl)-

		2,2,3,3,4,4,4-heptafluorobutanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propyl 2,2,3,3,4,4,4-heptafluorobutanoate
7D		
	31	1-((3-((3-(2-(2,5-dioxotetrahydrofuran-3-yl)acetoxy)-2-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)-3-(((((5S)-5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propan-2-yl 2-(2,5-dioxotetrahydrofuran-3-yl)acetate
8		
	32	4,4'-(((cyclohexane-1,3-diylbis(methylene))bis(oxy))bis(methylene))bis(1,3-dioxolan-2-one)
	33	1-((3-((3-((((5-amino-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-hydroxypropoxy)methyl)cyclohexyl)methoxy)-3-hydroxypropan-2-yl ((1,3,3,5-tetramethylcyclohexyl)methyl)carbamate
9		
	33	1-((3-((3-((((5-amino-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-hydroxypropoxy)methyl)cyclohexyl)methoxy)-3-hydroxypropan-2-yl ((1,3,3,5-tetramethylcyclohexyl)methyl)carbamate
	34	2-hydroxy-3-((3-((3-(((((1-hydroxy-3-((3-((2-hydroxy-3-((((5-((3-(2-hydroxy-3-(methacryloyloxy)propoxy)-3-oxopropyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)propan-2-yl)oxy)carbonyl)amino)methyl)-3,5,5-trimethylcyclohexyl)amino)propanoyl)oxy)propyl methacrylate
10		
	35	2-hydroxyethyl methacrylate
	36	2,2,3,4,4,4-hexafluorobutyl methacrylate
	37	((3,3'-(((21-hydroxy-5-(hydroxymethyl)-11,11,13,13,15,15-hexamethyl-3,24-dioxo-4,7,12,14,19,23-hexaoxa-2,25-diaza-11,13,15-trisilahexacosane-1,26-diyl)bis(5,5-dimethylcyclohexane-3,1-diyl))bis(azanediyl))bis(propanoyl))bis(oxy))bis(2-hydroxypropane-3,1-diyl) bis(2-methylacrylate)
	38	NIU-DMA hydrogel
11		
	34	2-hydroxy-3-((3-((3-(((((1-hydroxy-3-((3-((2-hydroxy-3-((((5-((3-(2-hydroxy-3-(methacryloyloxy)propoxy)-3-oxopropyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)propan-2-yl)oxy)carbonyl)amino)methyl)-3,5,5-

		trimethylcyclohexyl)amino)propanoyl)oxy)propyl methacrylate
	39	A name could not be generated for this structure.
12		
	40	1-((3-((3-((2,2,3,3,4,4,4-heptafluorobutanoyl)oxy)-2-((((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)-3-((((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamoyl)oxy)propan-2-yl 2,2,3,3,4,4,4-heptafluorobutanoate
12A		
	41	1-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-3-((3-((2-((((5-(2,2,3,3,4,4,4-heptafluoro-N-((4-methylene-1,3-dioxolan-2-yl)methyl)butanamido)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-3-((2,2,3,3,4,4,4-heptafluorobutanoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)propan-2-yl 2,2,3,3,4,4,4-heptafluorobutanoate
13		
	42	(4-((1-(methacryloyloxy)-3-((3-((3-(((((1-((3-((3-((((5-((3-(3-(methacryloyloxy)-2-(4-phosphonobutoxy)propoxy)-3-oxopropyl)(4-phosphonobutyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-(4-phosphonobutoxy)propoxy)methyl)cyclohexyl)methoxy)-3-(4-phosphonobutoxy)propan-2-yl)oxy)carbonyl)amino)methyl)-3,5,5-trimethylcyclohexyl)(4-phosphonobutyl)amino)propanoyl)oxy)propan-2-yl)oxy)butyl)phosphonic acid
14		
	43	A name could not be generated for this structure.
15		
	44	A name could not be generated for this structure.
16		
	45	2-((perfluorophenyl)methoxy)-3-((3-((3-((perfluorophenyl)methoxy)-2-((((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)propyl ((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamate
16A		
	46	2-((perfluorophenyl)methoxy)-3-((3-((3-((perfluorophenyl)methoxy)-2-((((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)((perfluorophenyl)methyl)amino)cyclohexyl)methyl)carb

		amoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)propyl ((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)((perfluorophenyl)methyl)amino)cyclohexyl)methyl)carbamate
17		
	47	3-((3-((3-(((((1-((3-((3-((((5-((3-(3-(methacryloyloxy)-2-((perfluorophenyl)methoxy)propoxy)-3-oxopropyl)((perfluorophenyl)methyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-2-((perfluorophenyl)methoxy)propoxy)methyl)cyclohexyl)methoxy)-3-((perfluorophenyl)methoxy)propan-2-yl)oxy)carbonyl)amino)methyl)-3,5,5-trimethylcyclohexyl)((perfluorophenyl)methyl)amino)propanoyl)oxy)-2-((perfluorophenyl)methoxy)propyl methacrylate
18		
	48	A name could not be generated for this structure.
19		
	49	2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl)oxy)-3-((3-((3-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl)oxy)-2-((((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamoyl)oxy)propoxy)methyl)cyclohexyl)methoxy)propyl ((1,3,3-trimethyl-5-(((4-methylene-1,3-dioxolan-2-yl)methyl)amino)cyclohexyl)methyl)carbamate
19A		
	50	3-((3-((2-((((5-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl)((4-methylene-1,3-dioxolan-2-yl)methyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamoyl)oxy)-3-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl)oxy)propoxy)methyl)cyclohexyl)methoxy)-2-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl)oxy)propyl ((5-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)dimethylsilyl)((4-methylene-1,3-dioxolan-2-yl)methyl)amino)-1,3,3-trimethylcyclohexyl)methyl)carbamate

[0068] The methods and compositions disclosed herein are exemplified by the following non-limiting examples.

EXAMPLES

Example 1

[0069] This example was prepared with the use of a 50:50 wt% blend of bisphenol A glycidyl methacrylate (Bis-GMA) and triethylene-glycol dimethacrylate (TEGDMA). Camphorquinone (CQ) (0.5wt%) and 2-(dimethylamino)ethyl methacrylate (DMAEMA) (0.5 wt%) were used as a photoinitiator and accelerator respectively. The formulated resin system was mixed thoroughly by stirring for 10 min under N_2 atmosphere. Formulation injected into mold system which made in a Teflon mold between two glass slides covered with transparent polyethylene film. Samples were irradiated with visible light curing unit (Rembrandt-Virtuoso Phase II) for 80 seconds on each of the two sides. The wavelength of the light was between 380 and 520 nm with maximal intensity at 470 nm and light intensity was 1500 mW/cm^2.

Example 2

[0070] This example was prepared with the use of a 50:50 wt% blend of bisphenol A glycidyl methacrylate (Bis-GMA) and triethylene-glycol dimethacrylate (TEGDMA). Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (1 wt%) were used as a photoinitiator. The formulated resin system was mixed thoroughly by stirring for 10 minutes under N_2 atmosphere. Formulation injected into mold system which made in a Teflon mold between two glass slides covered with transparent polyethylene film. Samples were irradiated with visible light curing unit (Rembrandt-Virtuoso Phase II) for 80 s on each of the two sides. The wavelength of the light was between 380 and 520 nm with maximal intensity at 470 nm and light intensity was 1500 mW/cm^2.

Example 3

[0071] This example was prepared with the use of a 50:50 wt% blend of nonisocyanate urethane dimethacrylate (NIPUDMA) and triethylene-glycol dimethacrylate (TEGDMA). Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Irgacure 819) (1 wt%) were used as a photoinitiator. The formulated resin system was mixed thoroughly by stirring for 10 min under N_2 atmosphere. Formulation injected into mold system which made in a Teflon mold between two glass slides covered with transparent polyethylene film. Samples were irradiated with visible light curing unit (Rembrandt-Virtuoso Phase II) for 80 s on each of the two sides. The wavelength of the light was between 380 and 520 nm with maximal intensity at 470 nm and light intensity was 1500 mW/cm^2.

Example 4

[0072] This example was prepared with the use of a 50:50 wt% blend of fluorinated nonisocyanate urethane dimethacrylate (NIPUDMA) and triethylene-glycol dimethacrylate (TEGDMA). Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (1 wt%) were used as a photoinitiator .The formulated resin system was mixed thoroughly by stirring for 10 min under N_2 atmosphere. Formulation injected into mold system which made in a Teflon mold between two glass slides covered with transparent polyethylene film. Samples were irradiated with visible light curing unit (Rembrandt-Virtuoso Phase II) for 80 s on each of the two sides. The wavelength of the light was between 380 and 520 nm with maximal intensity at 470 nm and light intensity was 1500 mW/cm^2.

[0073] The compositions from Examples 1 – 4 are shown in the Table 3.

Table 3

	Compositions (wt %)			
	Example 1 (parts per hundred)	Example 2 (parts per hundred)	Example 3 (parts per hundred)	Example 4 (parts per hundred)
Bis-GMA	50	50		
TEGDMA	50	50	50	50
NIPU			50	
FNIPU				50
CQ	0.5			
DMAEMA	0.5			
IRGACURE 819		1	1	1

The properties of the compositions of the Examples 1 – 4 are shown in the Tables 4 – 7.

Table 4: Water absorption study

Material	Water Absorption (m3-m2)/v $\mu g/mm^3$	Water solubility (m3-m1)/v $\mu g/mm^3$	Water Absorption (m3-m2)/m2) x100%	Water Solubility (m3-m2)/m2) x100 %
Example 1	47.8	4.25	4.06	0.37
Example 2	49.8	0.85	4.18	0.07
Example 3	112.7	2.1	9.26	0.19
Example 4			0.3	

Table 5: Contact angle-surface energy

Material	Sessile (H_20) (STDV)	MeI2 (STDV)	Surface energy (STDV) (mN/m)
Example 2	76 (2.5)	28(2.8)	47.49 (0.9)
Example 3	70 (1.2)	32(1.8)	48.7 (0.8)
Example 4	96 (2.0)	65 (1.0)	28.4 (0.3)

Table 6: DC % (Degree of conversion %)

	DC %
Example 2	56
Example 1	45.5
Example 3	76.5
Example 4	80.3

Table 7: Dynamic Mechanical Spectroscopy

		Run #1		Run #2	
		Storage Modulus (-50°C) (GPa)	Tan delta (°C)	Storage Modulus (-50°C) (GPa)	Tan Delta (°C)
Example 2	10 Hz	4.41	169	3.85	170
	1 Hz	4.21	159	3.93	161
	0.1 Hz	4.11	140	3.78	153
Example 2	10 Hz	4	172	4.12	174
	1 Hz	3.95	160	4	167
	0.1 Hz	3.7	140	3.88	157
Example 3	10 Hz	3.74	123	2.72	137
	1 Hz	3.74	111	2.64	125
	0.1 Hz	3.49	96	2.52	117
Example 3	10 Hz	3.2	125	2.91	140
	1 Hz	3.03	114	2.9	131
	0.1 Hz	2.9	99	2.84	120
Example 3	10 Hz	3.58	121		
	1 Hz	3.52	108		
	0.1 Hz	3.26	100		
Example 4	10 Hz	3.07	123	2.85	133
	1 Hz	2.94	111	2.72	124
	0.1 Hz	2.76	98	2.67	113
Example 4	10 Hz	3.28	130	2.74	133
	1 Hz	2.97	113	2.6	124
	0.1 Hz	2.76	100	2.56	113

[0074] From the Tables 4 – 7 above, it may be seen that the hydrophobicity of the surfaces increases with the fluorination of the dimethacrylate functionalized polyurethane. From the Table 6 it may be seen that the fluorination (Example 4) increases the contact angle substantially over that displayed by non-fluorinated dimethacrylate functionalized polyurethanes (See Examples 2 and 3). In addition, from the Table 7 it may be seen that the

introduction of fluorination (Example 4) reduces the glass transition temperature over that displayed by non-fluorinated dimethacrylate functionalized polyurethanes (See Examples 2 and 3). The second run in a dynamic mechanical analysis device increases the glass transition temperature by about 10 to 15 degrees Centigrade indicating increased crosslinking.

[0075] The hydrophobicity lends the group to use in dental restorations, protective coatings, hyrophobic fibers, dental coatings to prevent decay, wire coatings, paints, etc. The unique feature is the toughness of the urethane functionality and the ability to add many different reactive groups including amines, epoxides, maleic anhydride and related functionalities to enable polymerization with radical dependent reactions. Thiol groups may be used to enhance reactions in radical polymerizations as well protective coatings for gold.

[0076] In one embodiment, the fluorinated urethane, the phosphorylated urethane, sulfonated urethane or the anhydride terminated urethane detailed above may be blended with a polymeric resin. Polymeric resins listed above may be used. It may also be used to coat polymeric, metallic or ceramic substrates. The fluorinated urethane, the phosphorylated urethane, sulfonated urethane or the anhydride terminated urethane may be crosslinked by radiation or by the use of thermal energy and can be used in coatings, dental resins, thermosetting resins, or the like.

[0077] While this disclosure describes exemplary embodiments, it will be understood by those skilled in the art that various changes can be made and equivalents can be substituted for elements thereof without departing from the scope of the disclosed embodiments. In addition, many modifications can be made to adapt a particular situation or material to the teachings of this disclosure without departing from the essential scope thereof. Therefore, it is intended that this disclosure not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this disclosure.

[0078] What is claimed is:

CLAIMS

1. A composition comprising:

a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof.

2. The composition of Claim 1, having any one of the structure of Figures 12 through 19.

3. The composition of Claim 1, where the urethane is a fluorinated urethane dimethacrylate.

4. The composition of Claim 3, where the fluorinated urethane methacrylate is further functionalized with molecules that contain phosphorus, silicon and/or sulfur.

5. The composition of Claim 1, where the urethane comprises a polymer; and where the polymer is a polyolefin, a polycarbonate, a polyalkylene glycol, a polyester-carbonate, a polysiloxane, a polycarbonate-siloxane, a poly(meth)acrylate, a poly(meth)acrylate-siloxane, a polyalkyl(meth)acrylate, a polyalkyl(meth)acrylate-siloxane, a polyetherketone, a polysulfone, a polyphosphazene, a polyphosphonate, a polyimide, a polyetherimide, a polyacetal, a polyacrylic, a polystyrene, a polyester, a polyamide, a polyamideimide, a polyarylate, a polyarylsulfone, a polyethersulfone, a polyphenylene sulfide, a polyvinyl chloride, a polyfluoroethylene, a polyether etherketone, a polyether ketone ketone, a polybenzoxazole, a polyoxadiazole, a polybenzothiazinophenothiazine, a polybenzothiazole, a polypyrazinoquinoxaline, a polypyromellitimide, a polyquinoxaline, a polybenzimidazole, a polyoxindole, a polyoxoisoindoline, a polydioxoisoindoline, a polytriazine, a polypyridazine, a polypiperazine, a polypyridine, a polypiperidine, a polytriazole, a polypyrazole, a polypyrrolidine, a polycarborane, a polyoxabicyclononane, a polydibenzofuran, a polyphthalide, a polyanhydride, a polyvinyl ether, a polyvinyl thioether, a polyvinyl alcohol, a polyvinyl ketone, a polyvinyl halide, a polyvinyl nitrile, a polyvinyl ester, a polysulfonate, a polysulfide, a polythioester, a polysulfonamide, a polyurea, a polyphosphazene, a polysilazane, or a combination thereof.

6. The composition of Claim 1, where the urethane comprises a polymer.

7. The composition of Claim 1, where the urethane is crosslinked.

8. A composition comprising:

a urethane of the Figure 3; where hydroxyl or amine linkages of the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms,

sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof; and

a polymeric resin.

9. An article comprising:

a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof; and

a substrate upon which the fluorinated urethane methacrylate is disposed.

10. A method comprising:

reacting a cyclic carbonate with a diamine to form a urethane;

reacting the urethane with a methacrylate to form a non-isocyanate urethane methacrylate; and

functionalizing the non-isocyanate urethane methacrylate with a molecule that contains fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof.

11. The method of Claim 10, where the non-isocyanate urethane methacrylate is a fluorinated non-isocyanate urethane dimethacrylate.

12. An article comprising:

a urethane of the Figure 3; where hydroxyl or amine linkages on the urethane of the Figure 3 are functionalized with molecules that contain fluorine atoms, phosphorus atoms, sulfur atoms, unsaturated carboxylic acids, derivatives of unsaturated carboxylic acids, or combinations thereof.

13. The article of Claim 12, where the article is a dental resin, a fiber, a fiber coating, an abrasion resistant coating, or a coating for controlling hydrophobicity.

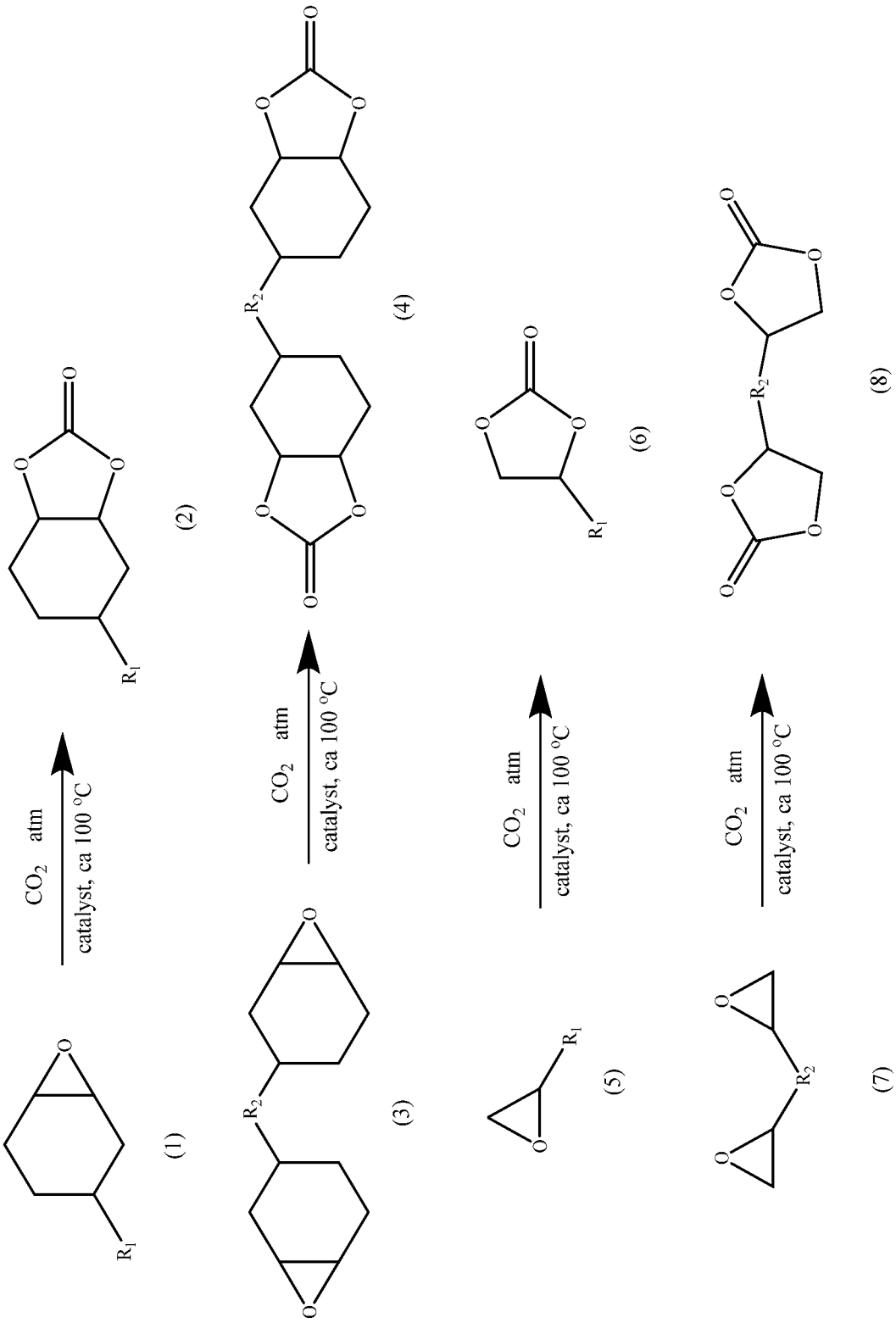


Figure 1

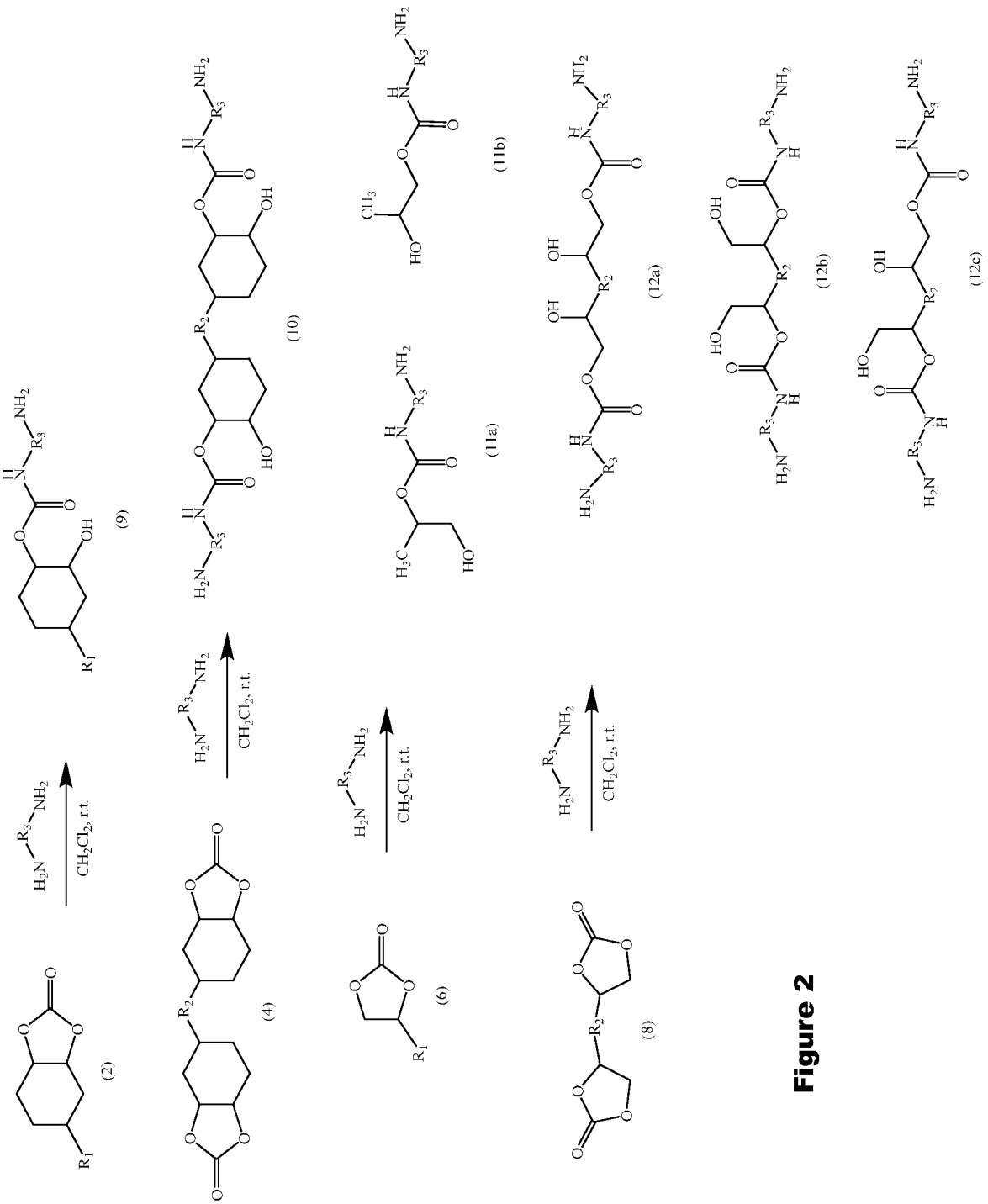


Figure 2

Figure 3

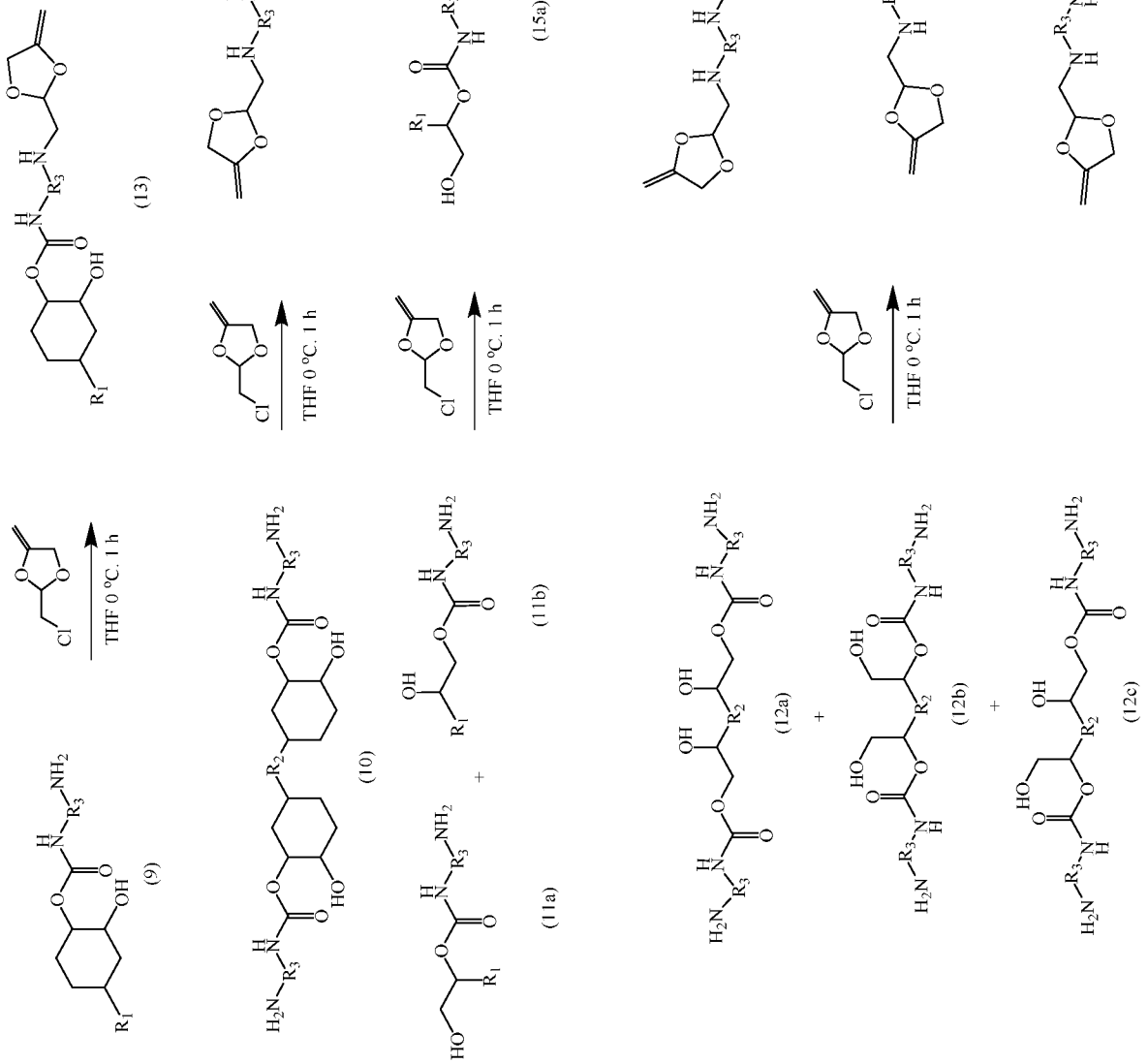
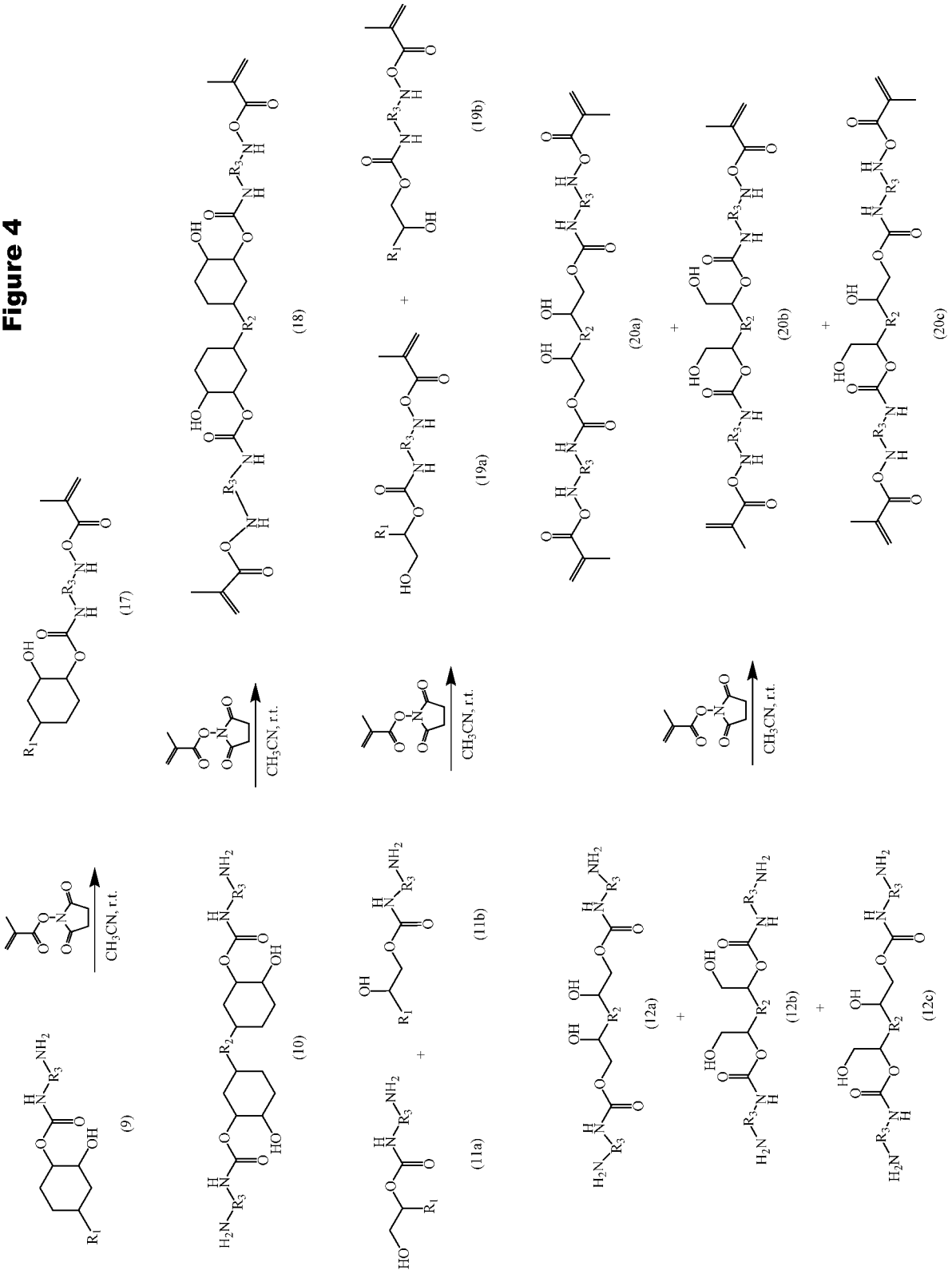


Figure 4



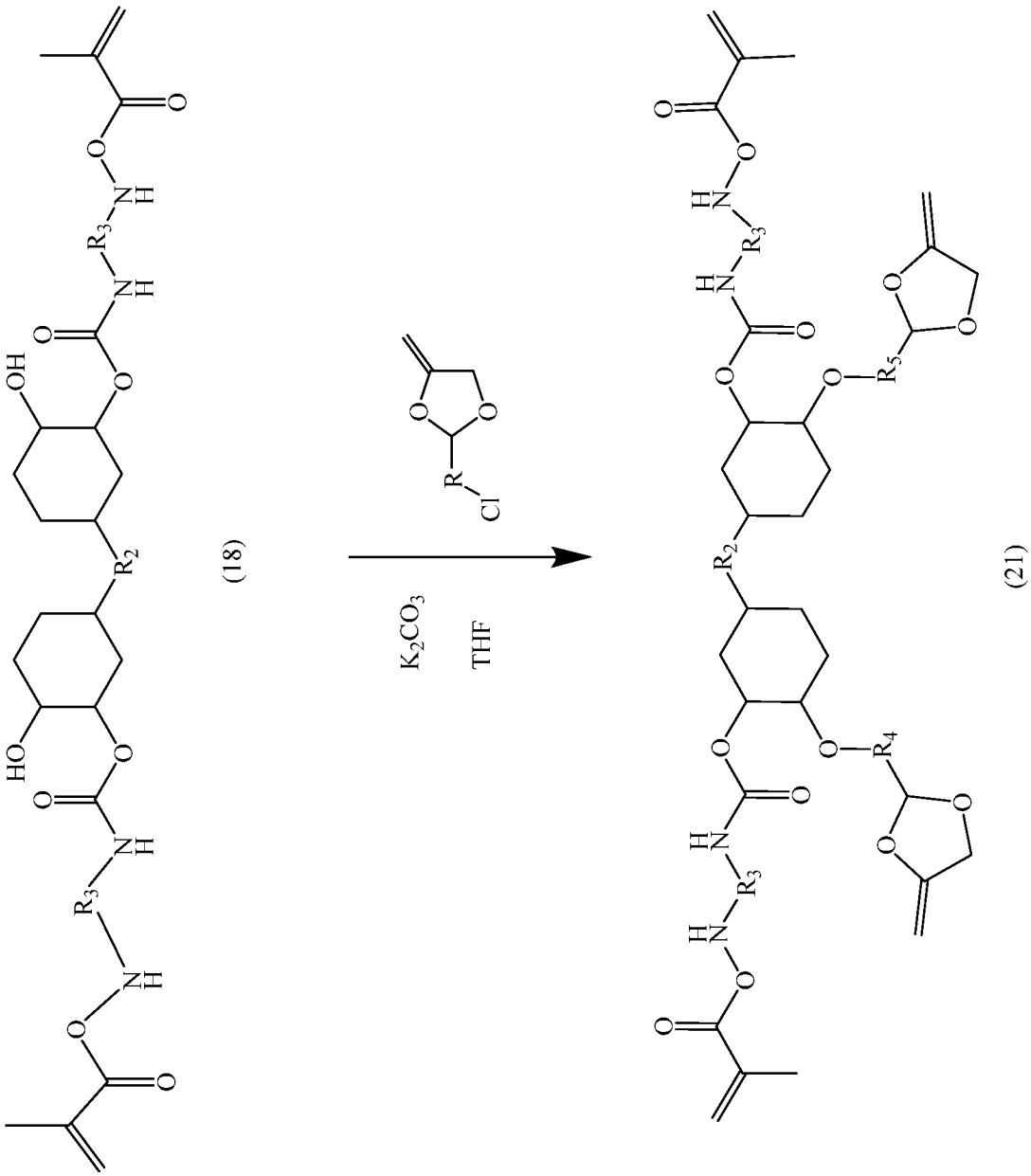


Figure 5

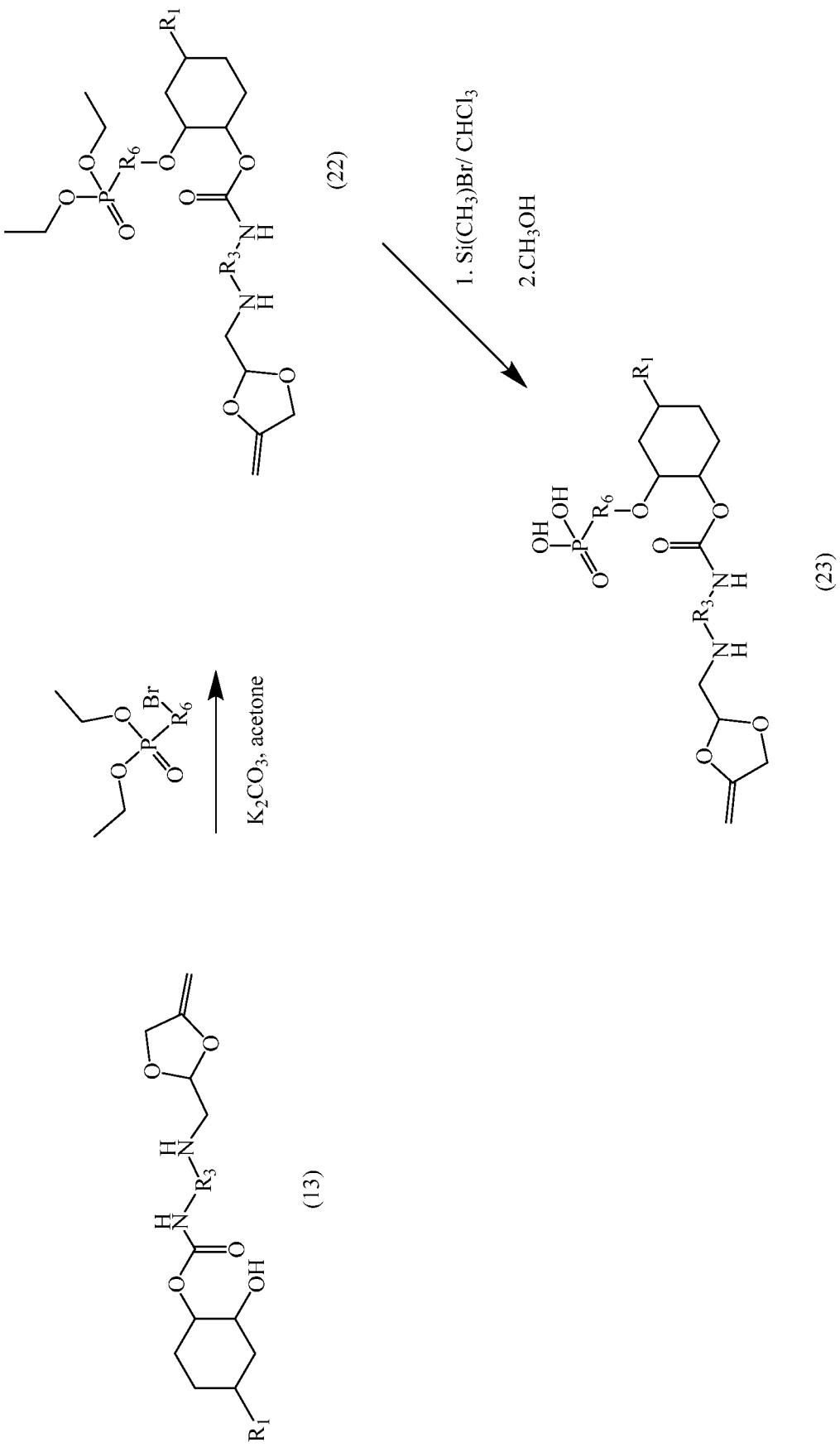


Figure 6

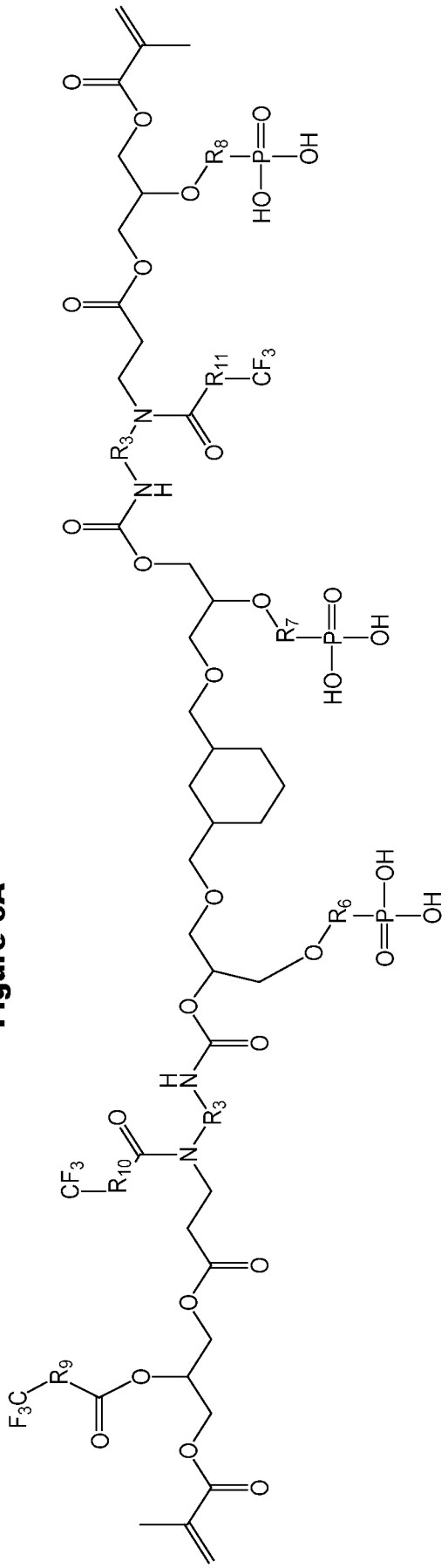


Figure 6A

(24)

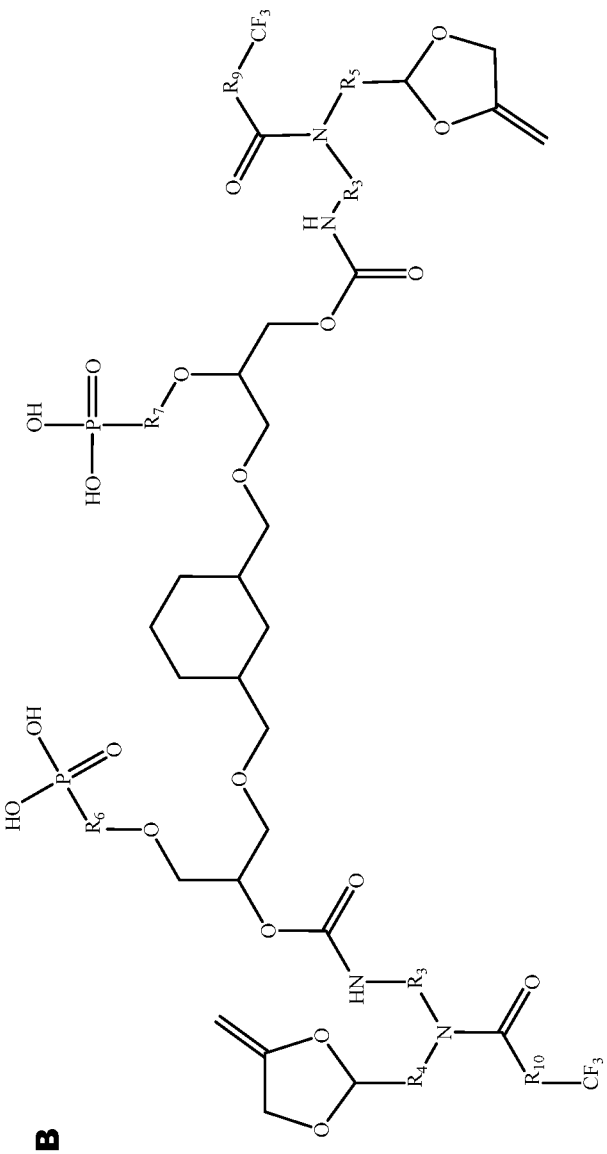


Figure 6B

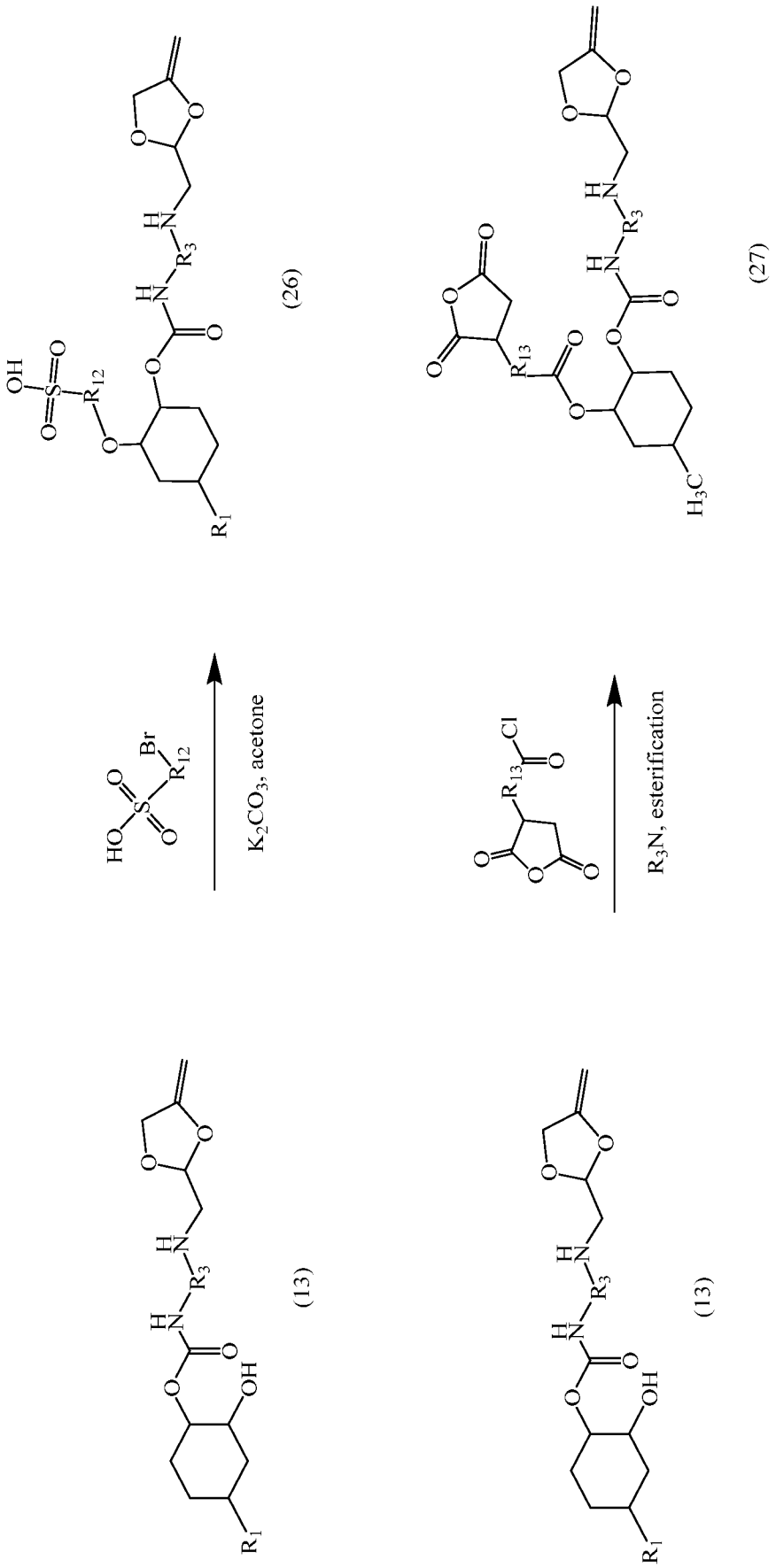
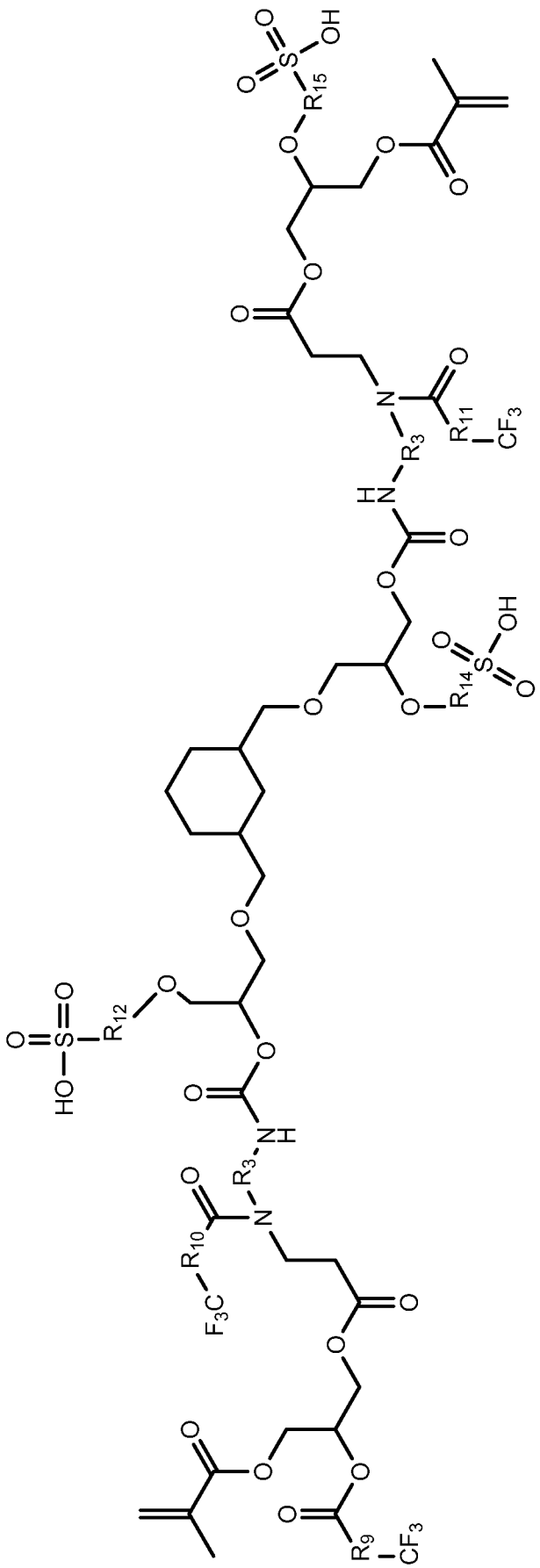
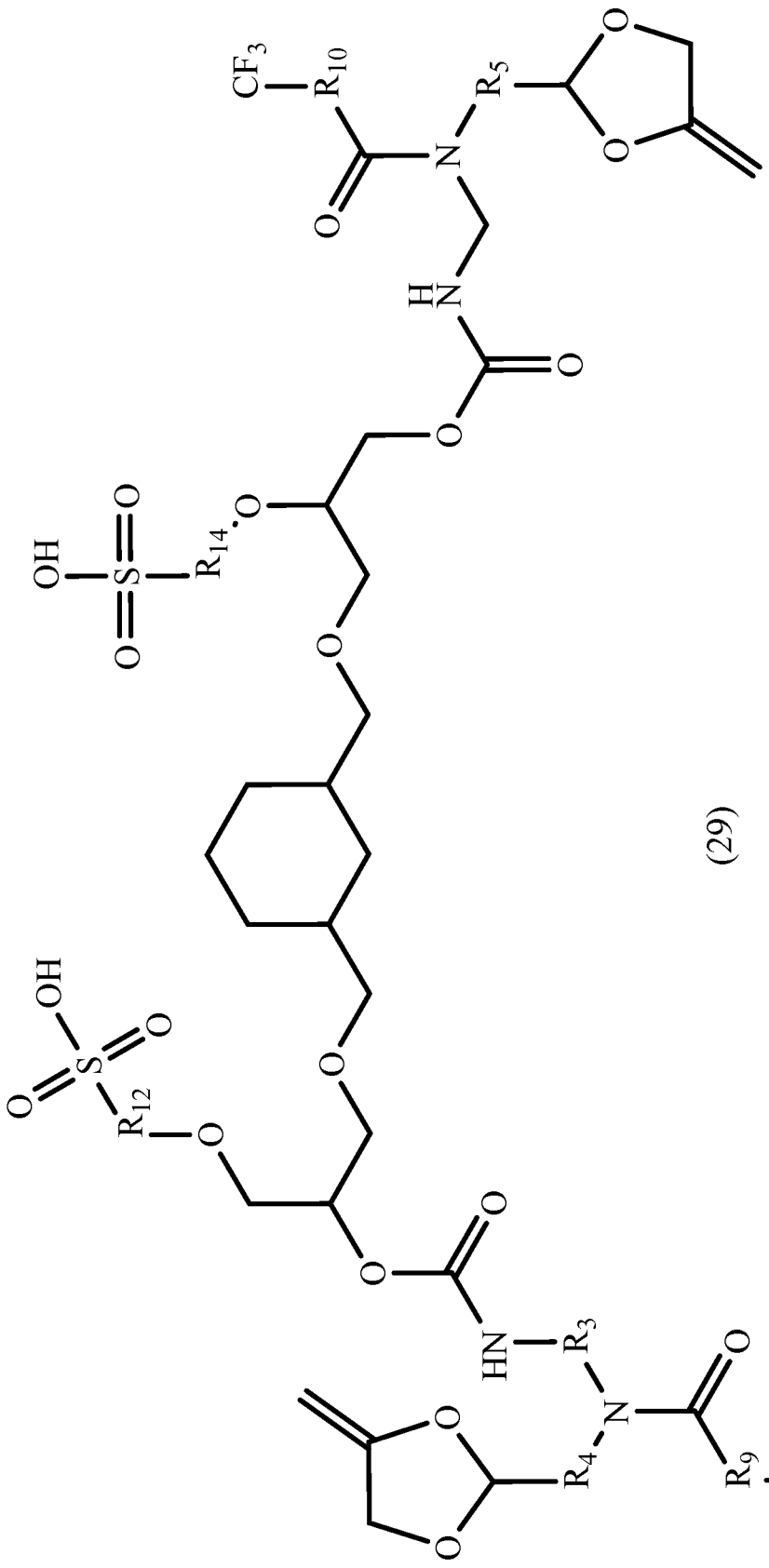


Figure 7



(28)

Figure 7A



(29)

Figure 7B

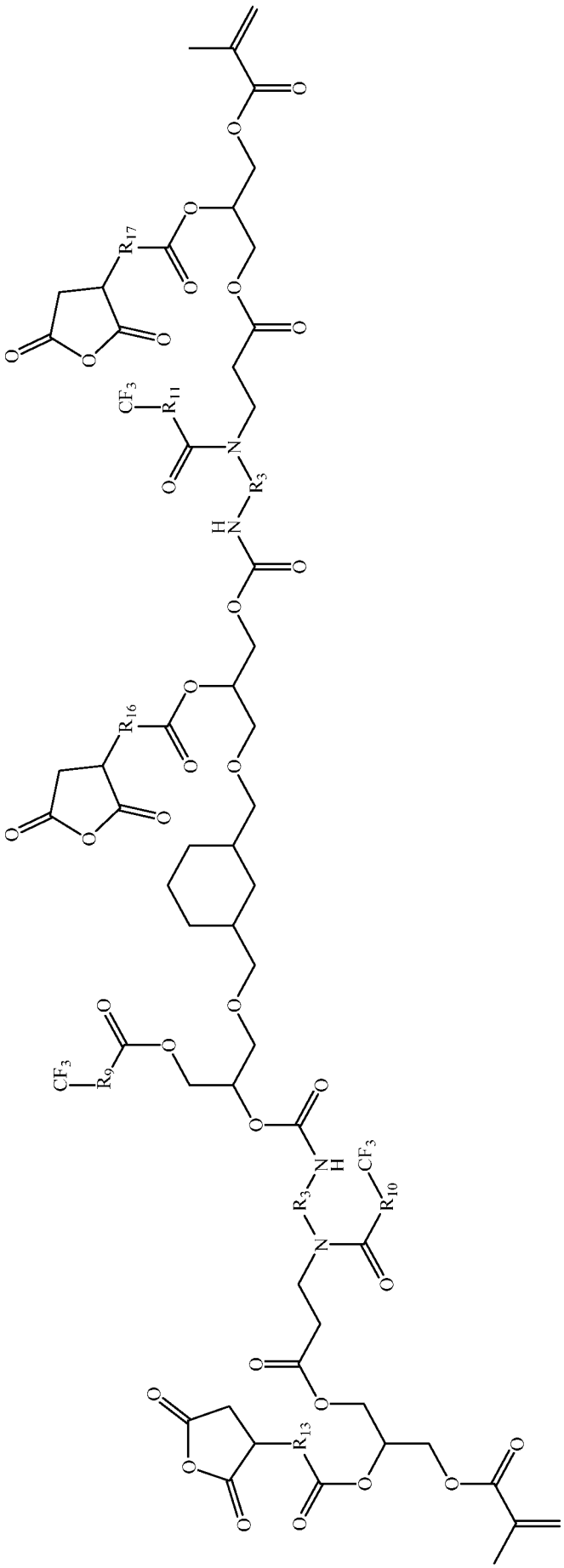
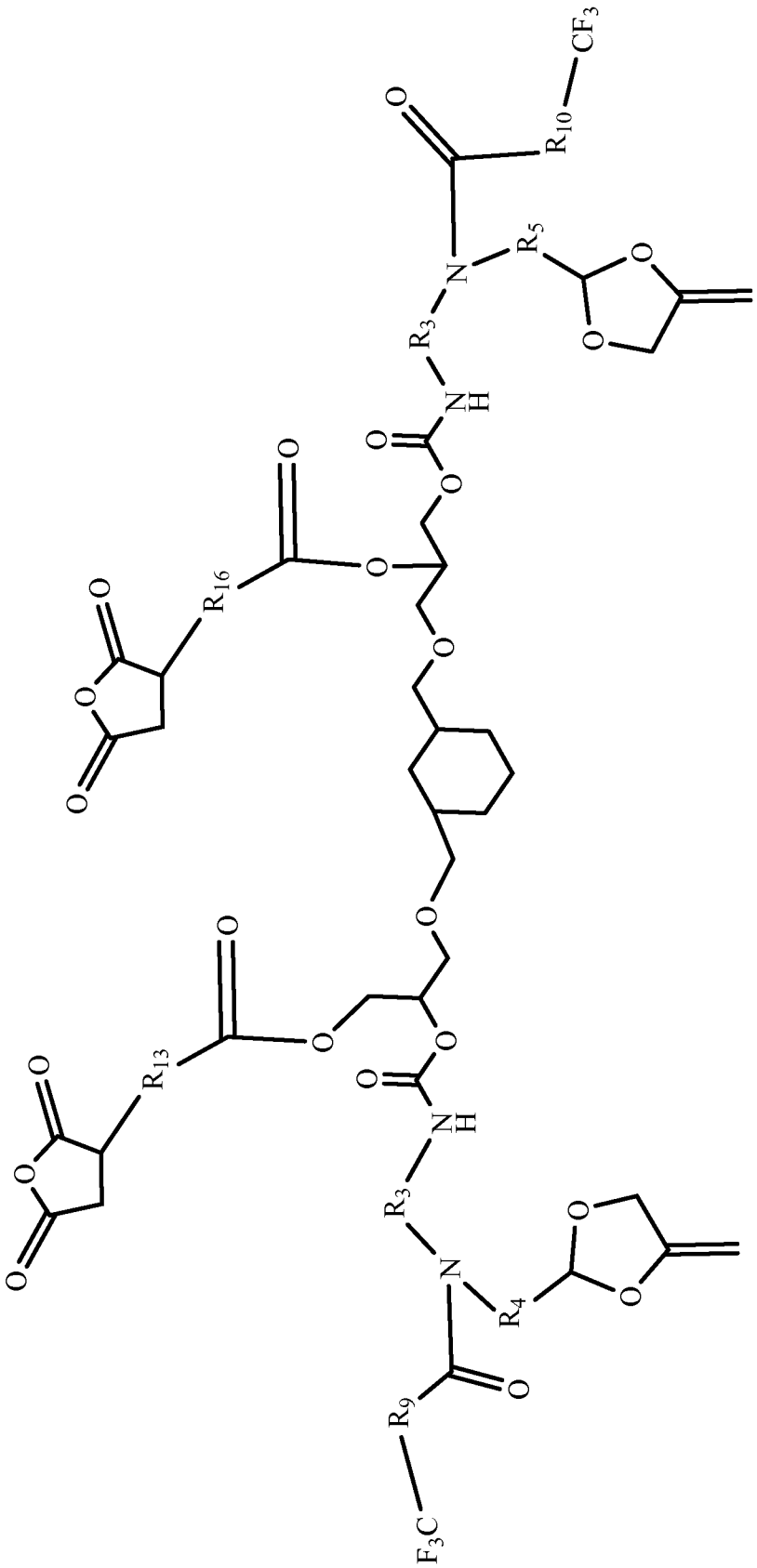


Figure 7C



(31)

Figure 7D

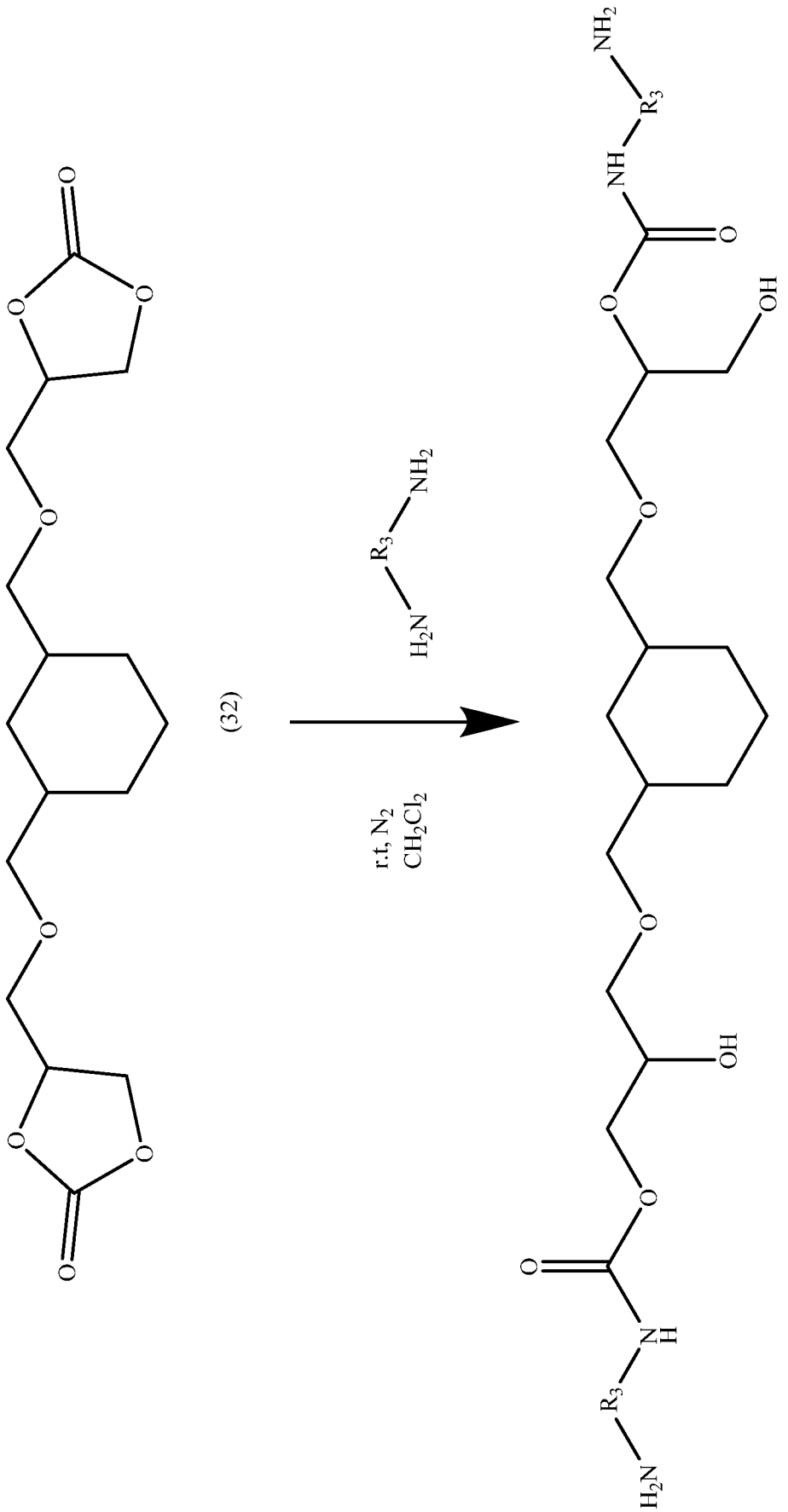


Figure 8

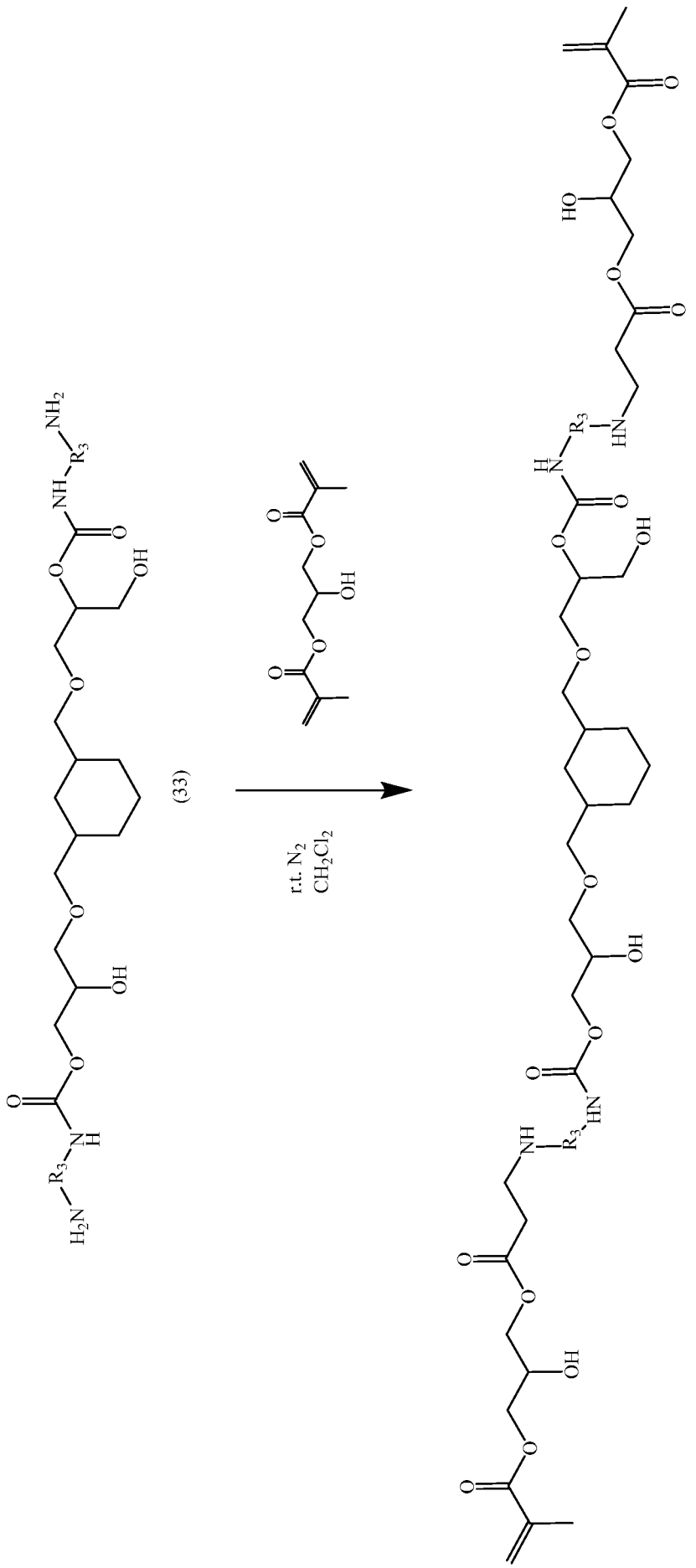


Figure 9

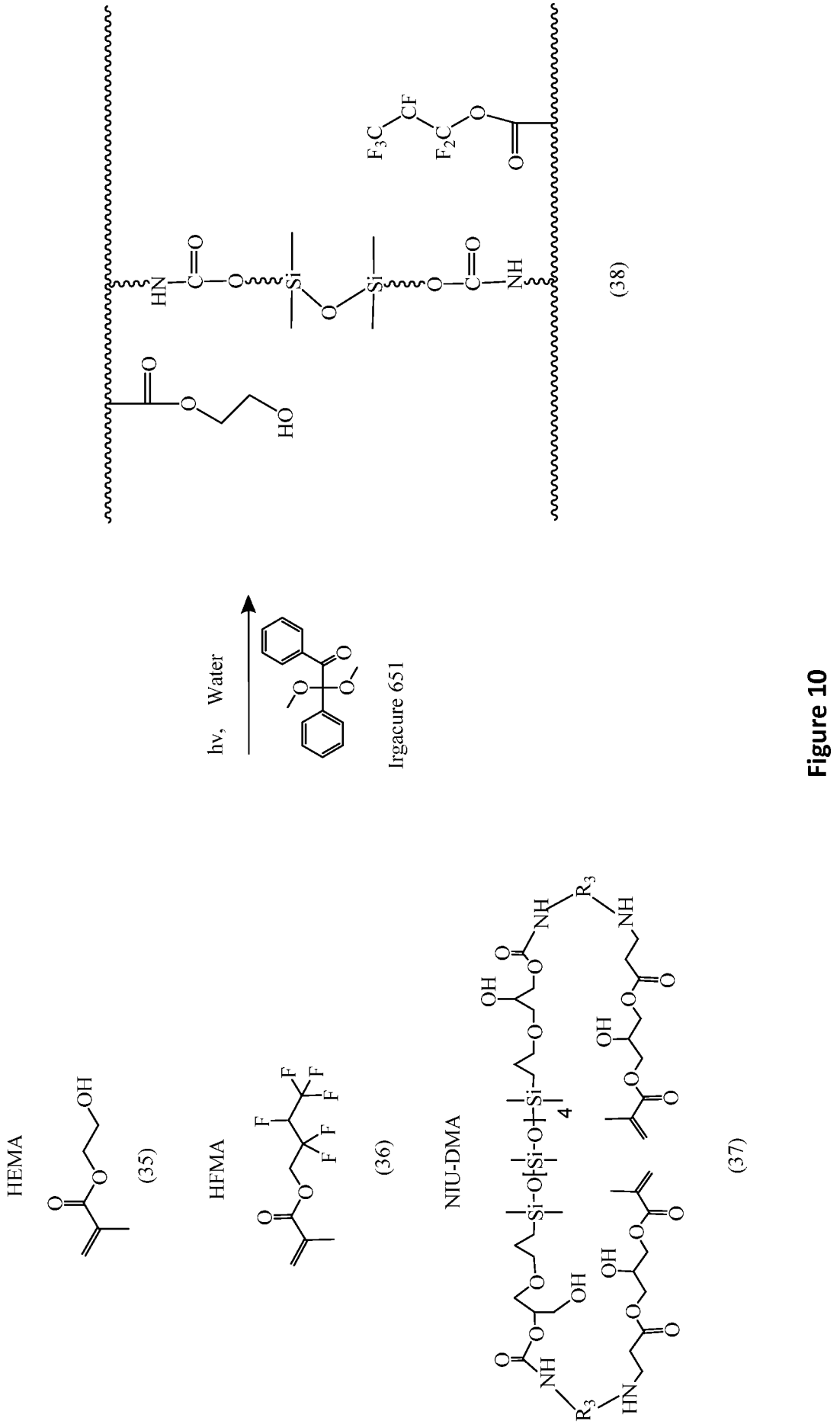
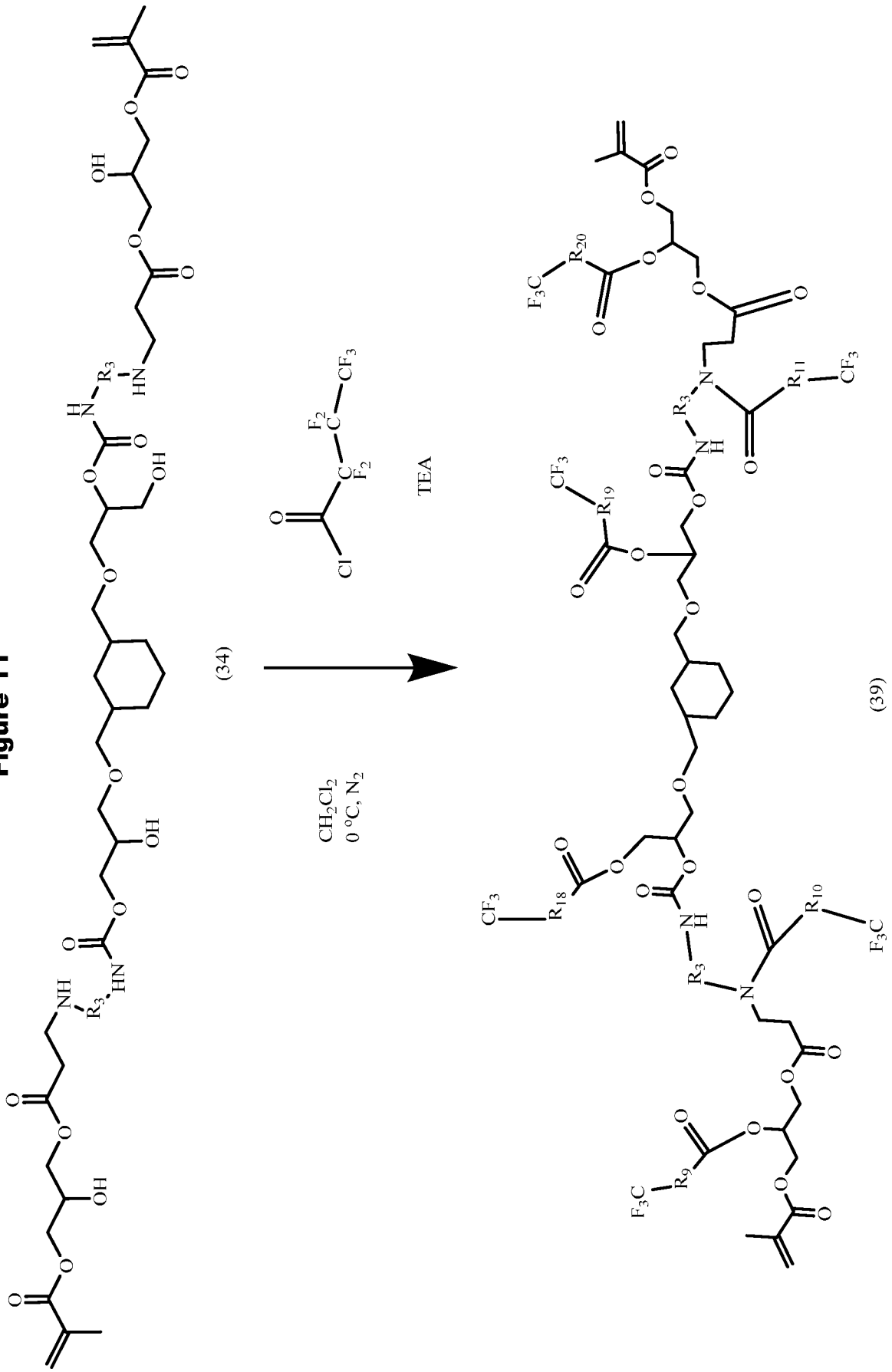


Figure 10

Figure 11



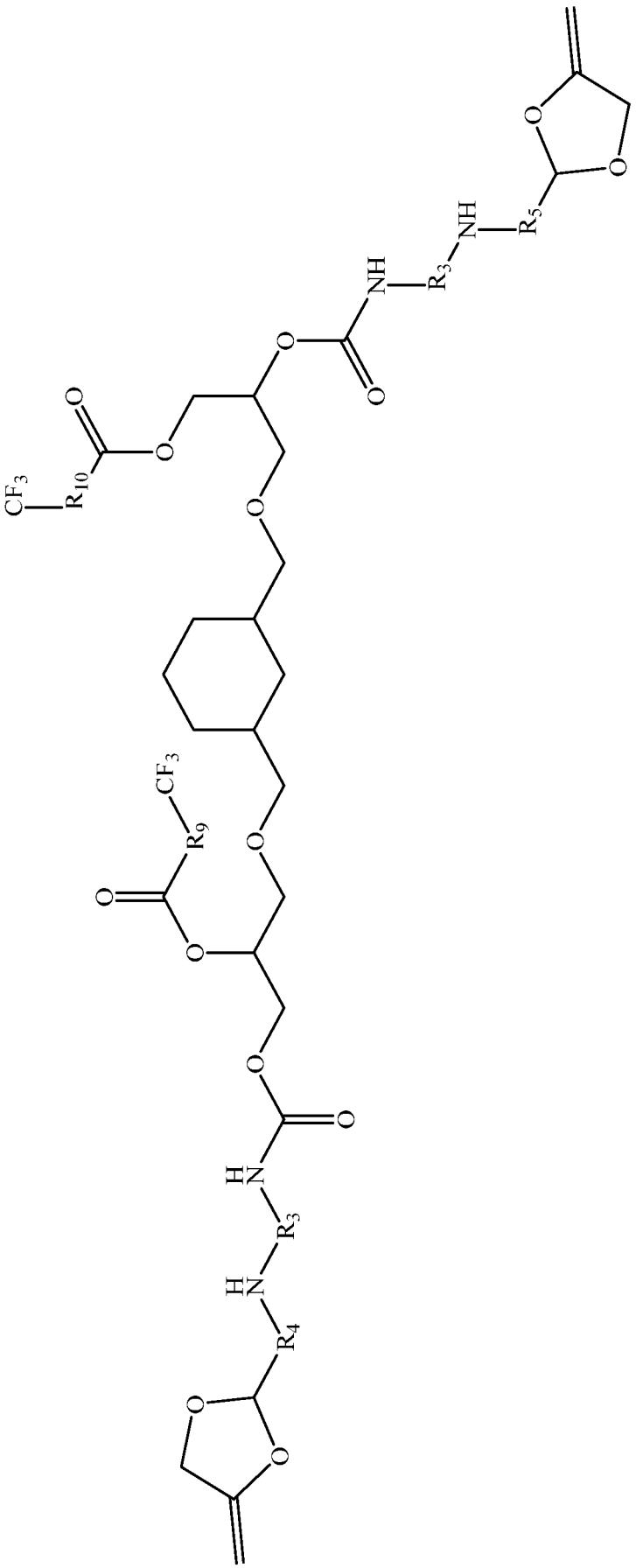
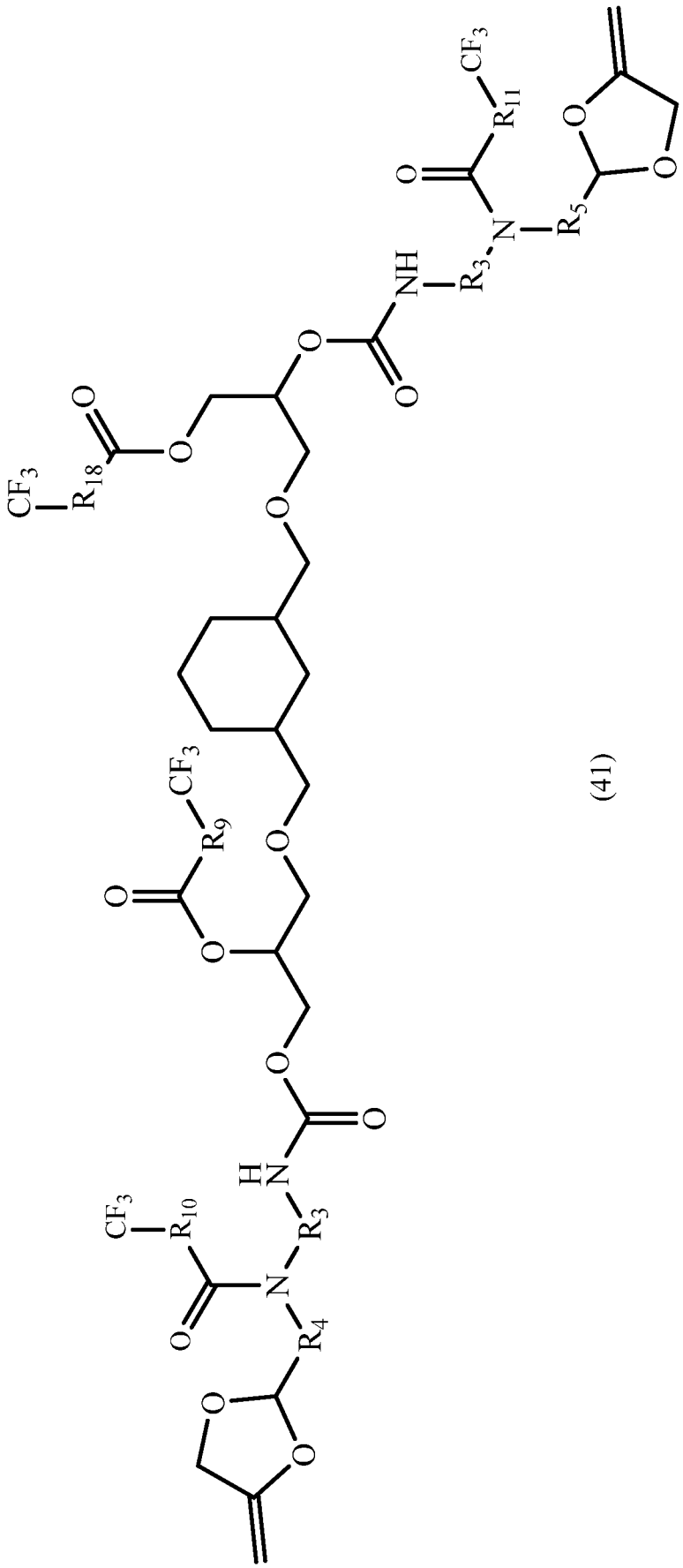


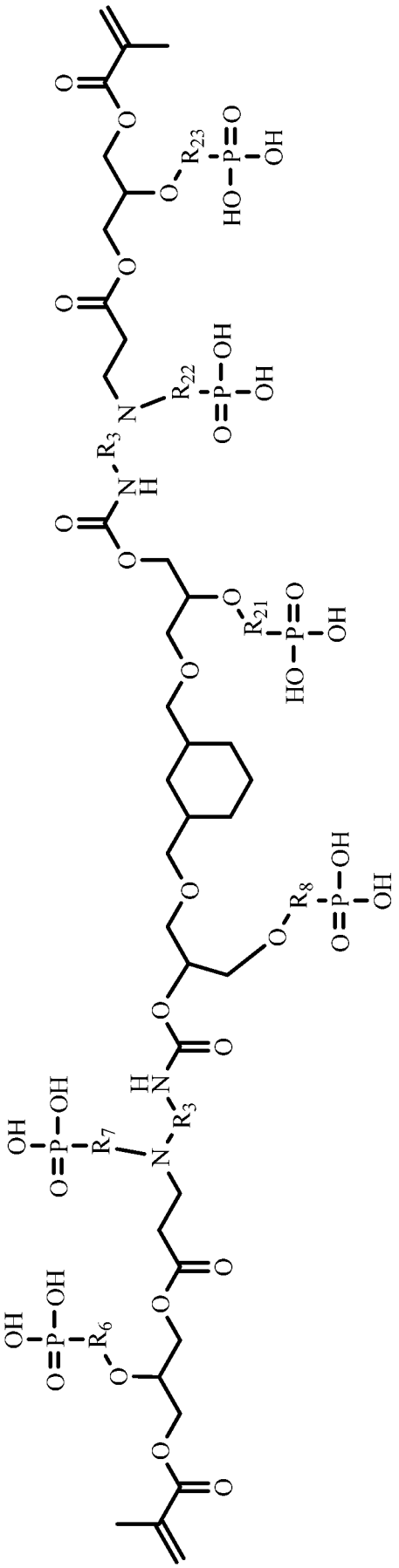
Figure 12



(41)

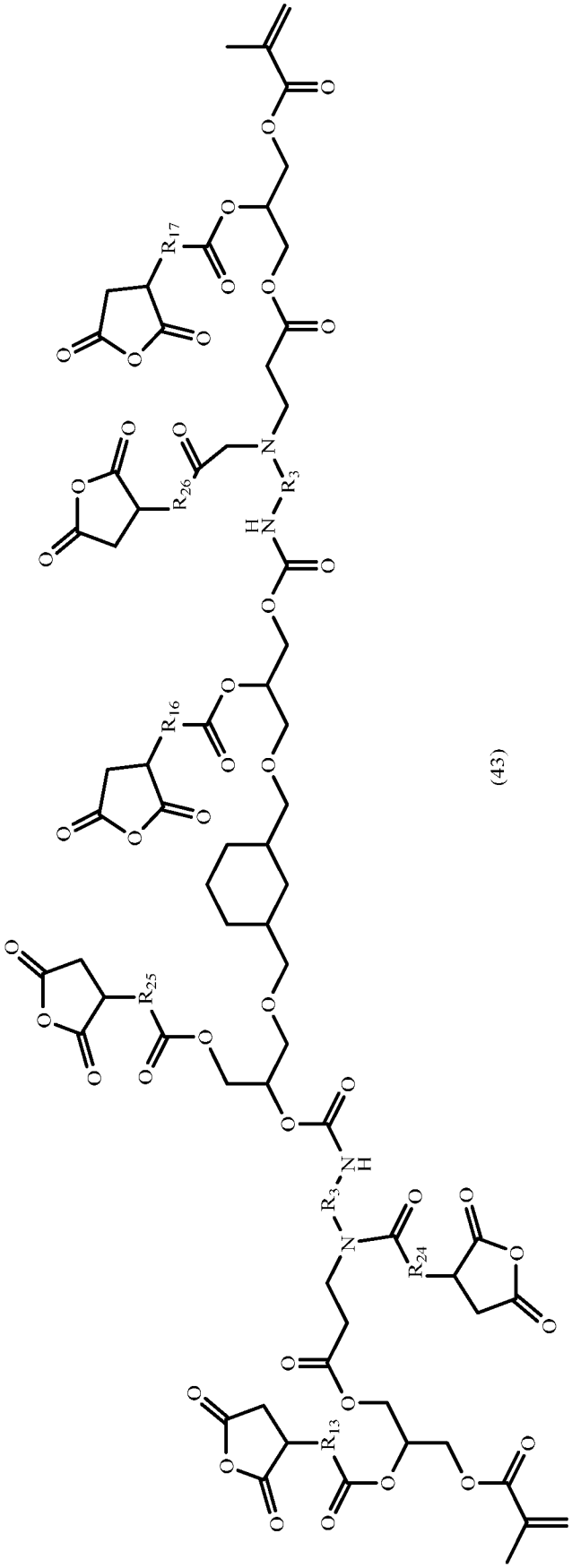
Figure 12A

Figure 13

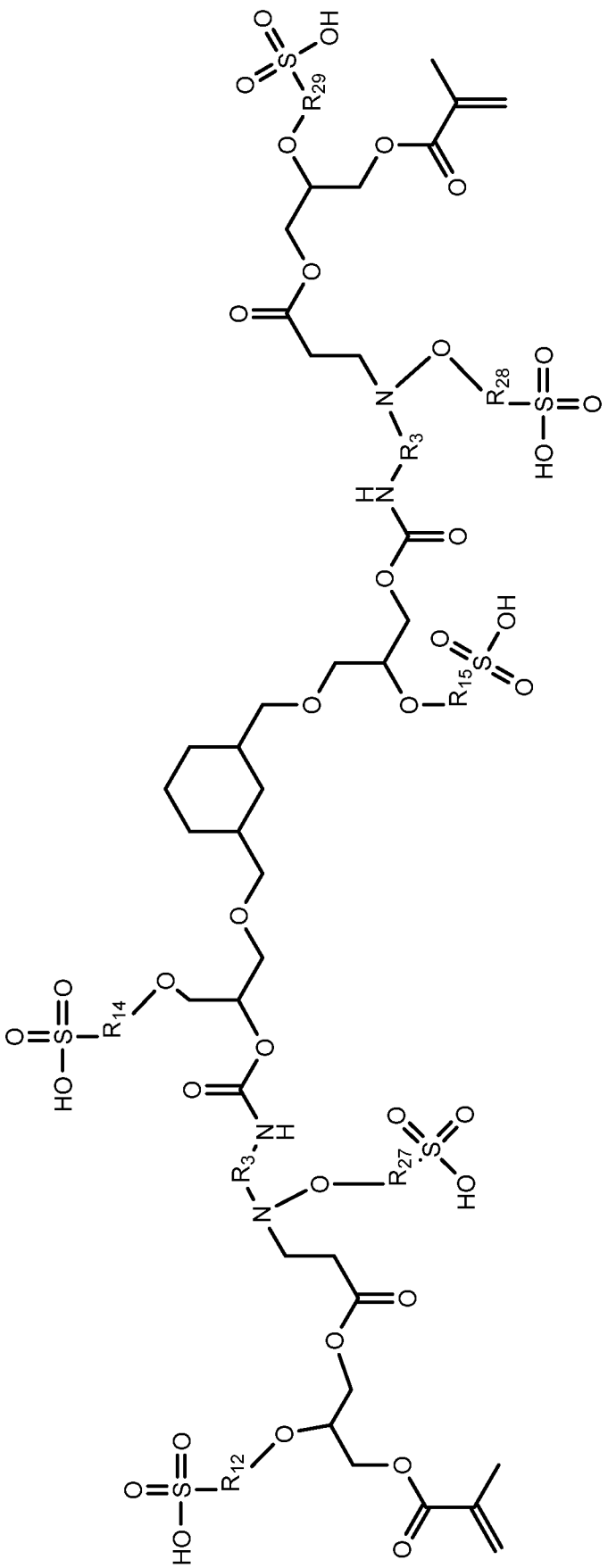


(42)

Figure 14

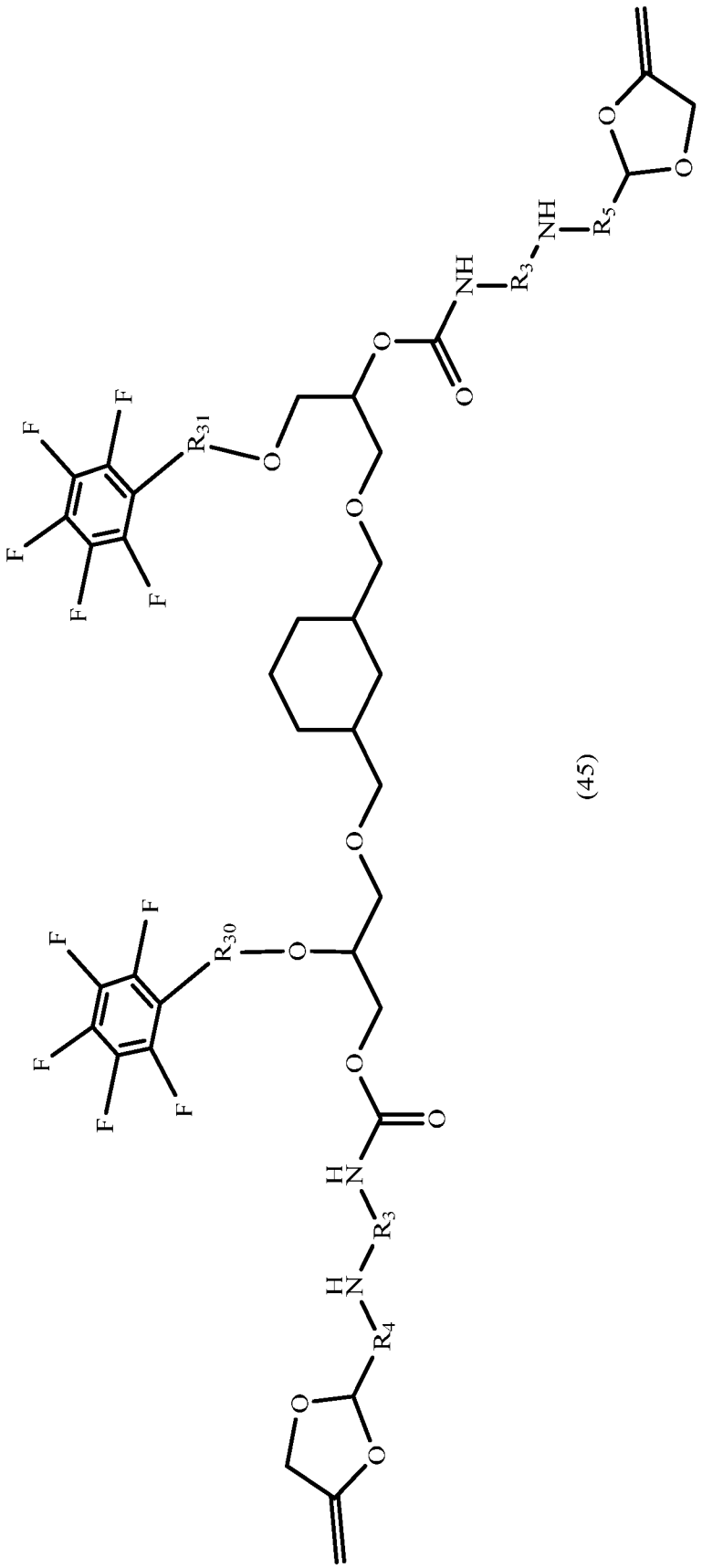


(43)



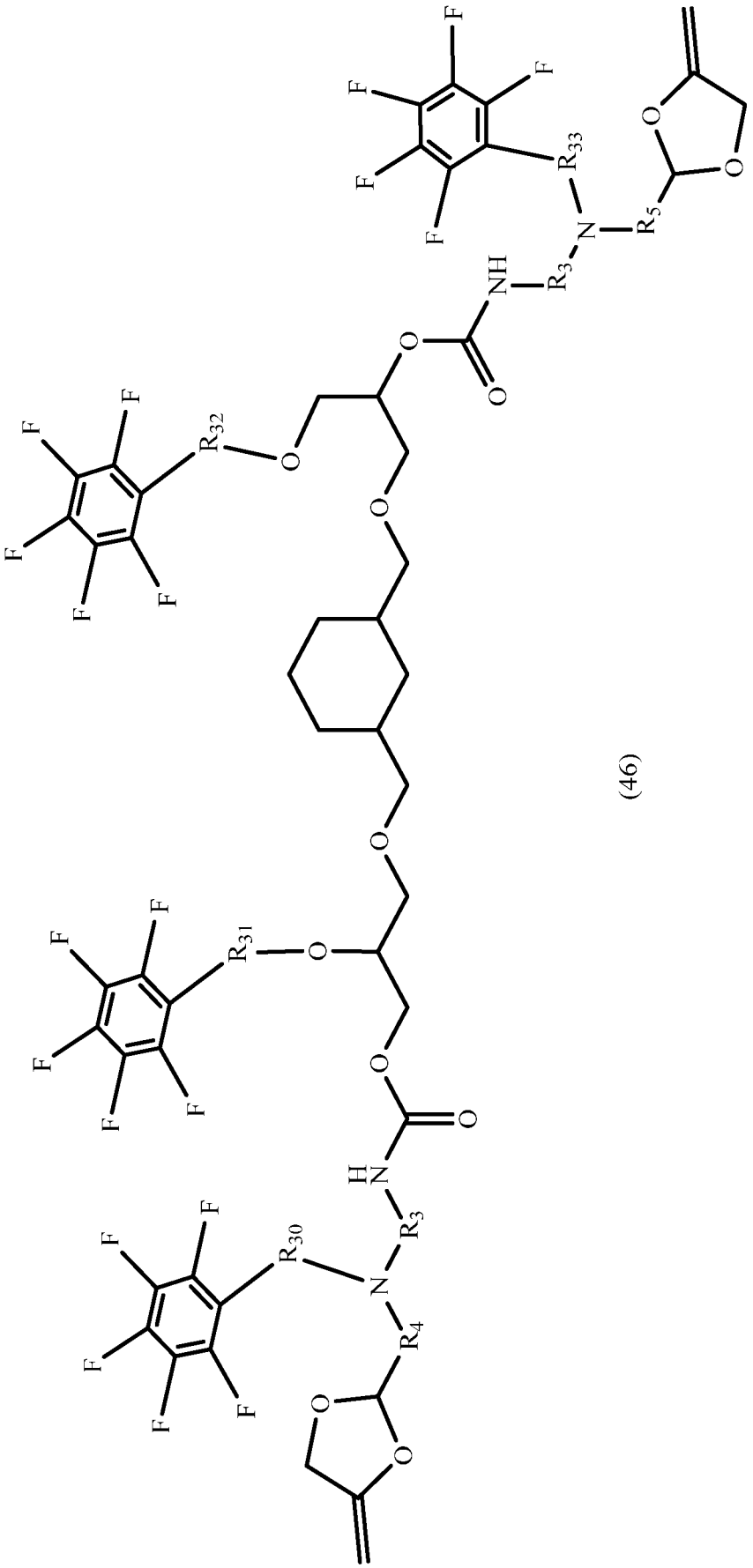
(44)

Figure 15



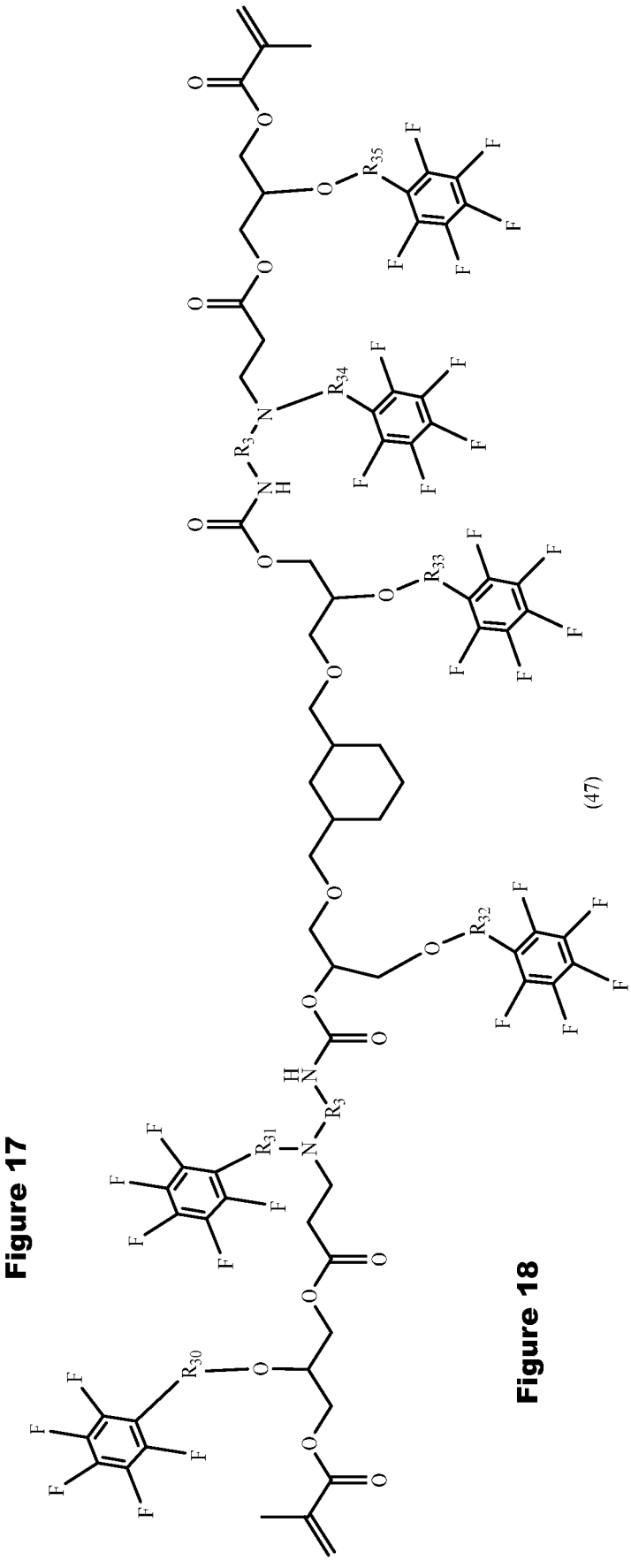
(45)

Figure 16



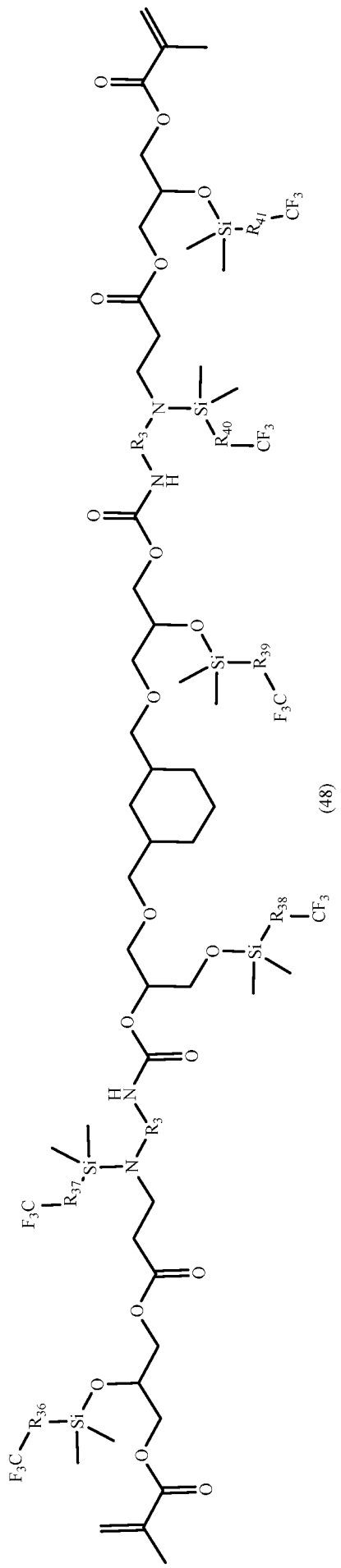
(46)

Figure 16A



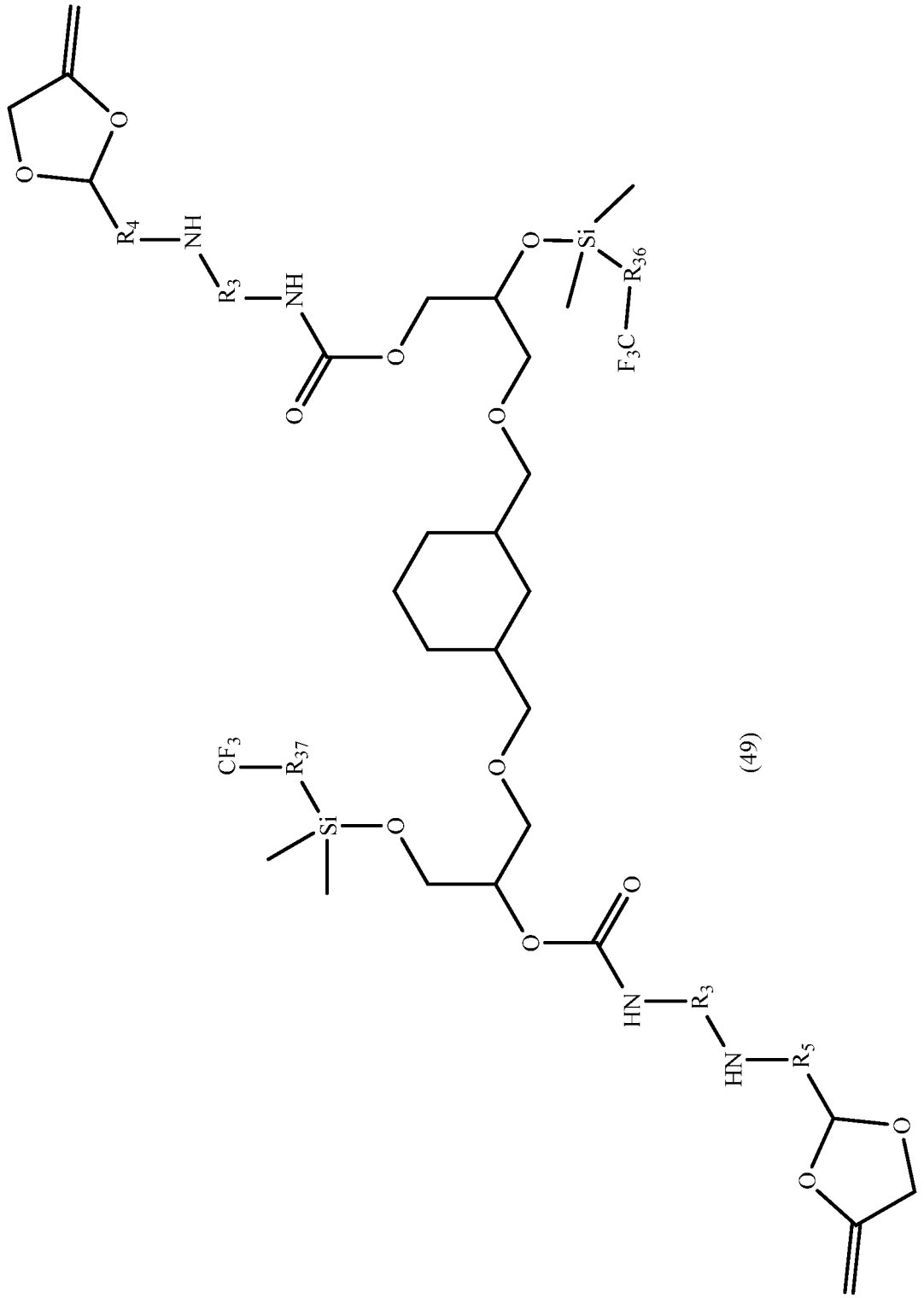
(47)

Figure 17



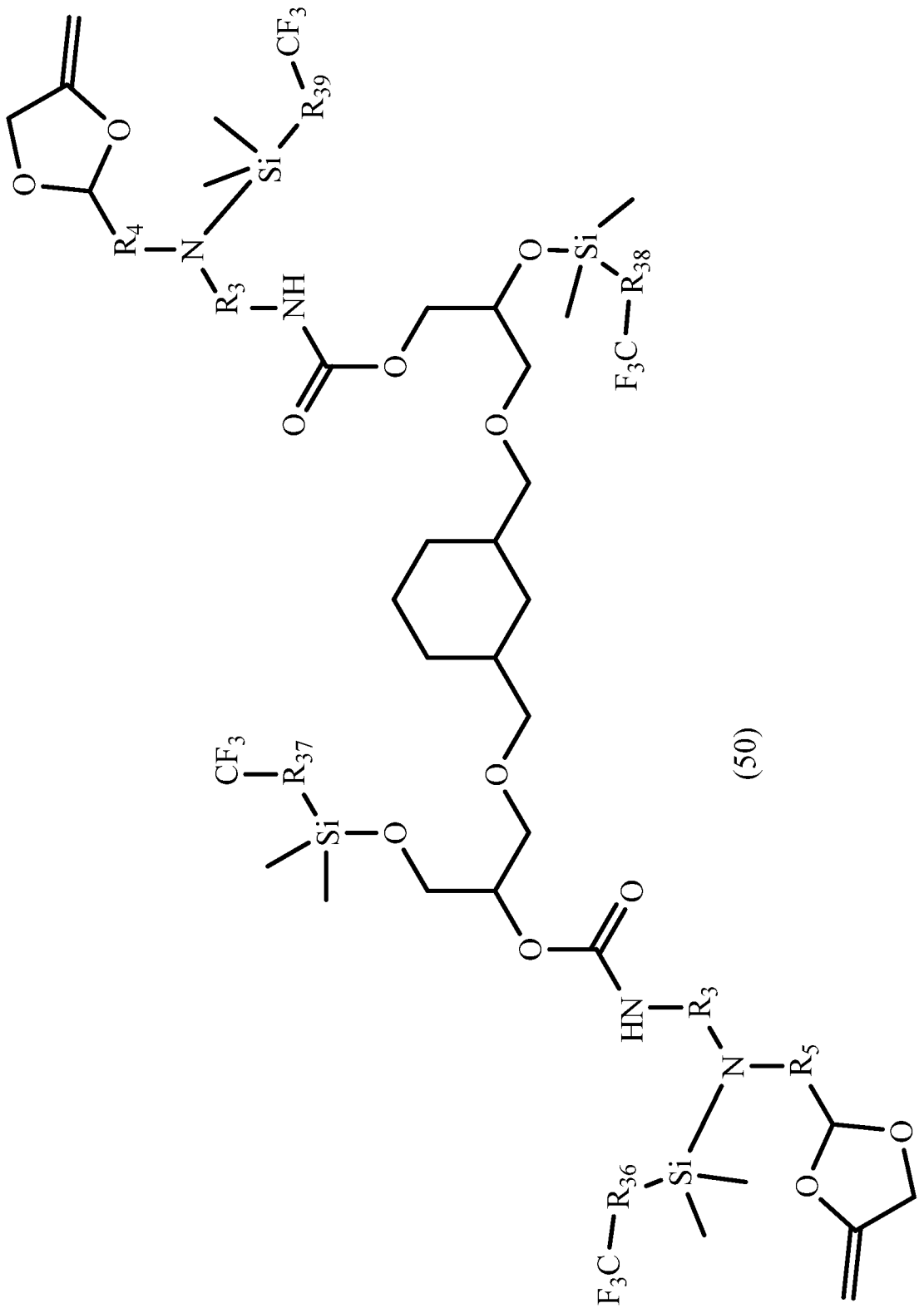
(48)

Figure 18



(49)

Figure 19



(50)

Figure 19A

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/37626

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08J 3/28; B05D 3/02 (2015.01)
CPC - B05D 1/18, 3/067
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(8): C08J 3/28; B05D 3/02 (2015.01)
CPC: B05D 1/18, 3/067

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; Scifinder; Google/Google Scholar; KEYWORDS: polyurethane, article, linkage, functional, fluorine, methacrylate, polymer, crosslink, resin, cyclic, carbonate, coating

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006/0058549 A1 (STONE, V et al.) 16 March 2006; paragraphs [0002], [0006], [0008], [0011]-[0012], [0014], [0016]-[0017], [0023]-[0025], [0030], [0044], [0058], [0152]	1-13
Y	US 2013/0004677 A1 (HWANG, JZ et al.) 03 January 2013; paragraphs [0010], [0012], [0014]-[0016], [0025], [0052]	1-13
Y	US 2007/0287093 A1 (JING, N et al.) 13 December 2007; paragraphs [0020], [0028], [0043]	3-4, 11
A	US 2005/0075471 A1 (FAN, WW et al.) 07 April 2005; entire document	1-13
A	US 2005/0095933 A1 (KIMBRELL, WC et al.) 05 May 2005; entire document	1-13
A	US 2010/0292396 A1 (BINDER, H et al.) 18 November 2010; entire document	1-13
A	US 2004/0024110 A1 (HAMERSKY, MW et al.) 05 February 2004; entire document	1-13

☐ Further documents are listed in the continuation of Box C. ☐ 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
20 August 2015 (20.08.2015)	30 SEP 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)