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(54) Title: PHOTOPOLYMER-BASED DIELECTRIC MATERIALS AND METHODS OF PREPARATION AND USE THEREOF

(57) Abstract: Photopolymer-based dielectric materials are provided with methods for preparing the same. Composites and electronic devices including such dielectric materials also are provided.

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PHOTOPOLYMER-BASED DIELECTRIC MATERIALS AND METHODS OF PREPARATION AND USE THEREOF

Introduction

[0001] The development of polymeric dielectric materials has been fundamental for the progress of organic electronic devices. In particular, emerging display and identification/tracking/labeling technologies based on organic thin-film transistors (OTFTs), such as electronic paper and radiofrequency identification (RFID) devices, require fabrication of OTFTs on plastic, paper, or other flexible substrates over very large areas and via high throughput processes. Therefore, there has been considerable effort in developing new materials for OTFT components (semiconductor, dielectric, and contacts) which can be deposited via solution-processing methods such as spin-coating, casting, and printing.

[0002] Although various polymers have been employed as dielectrics for OTFTs, several limitations of current-generation polymeric dielectric-based OTFTs exist. First, the leakage current densities of conventional polymeric dielectric films are relatively high (usually $> 1\times10^{-7}$ A/cm^2 at 2 MV/cm, $>> 1\times10^{-5}$ A/cm^2 at 4 MV/cm). Second, very few polymeric dielectric materials are sufficiently soluble to be solution-processed, especially via inexpensive printing techniques. Among those that are solution-processable, they often cannot survive the conditions used in subsequent solution-processing steps (e.g., for TFT device fabrication, the deposition of overlying layers such as the semiconductor layer (for bottom-gate devices), the conductor layer, and the passive layers), hence their application in device fabrication is significantly limited. Third, currently available polymeric dielectric materials often fail to achieve a sub-nanometer/nanometer surface smoothness, which is a prerequisite for stable TFT performance and operation.

[0003] To address these issues, crosslinkable polymeric dielectrics such as crosslinked melamine/Cr^{6+} salts-polyvinylphenol (PVP) and crosslinked benzocyclobutene (BCB) have been introduced. However, these polymer films require high annealing temperatures and their leakage current densities are usually higher than 10^{-7} A/cm^2 at 2 MV/cm. The high current leakage densities of these polymeric dielectrics are believed to be due to, among other factors, the hydrophilic nature of phenol-based polymers and the presence of crosslinker additives.

[0004] On the other hand, polymers with a hydrophobic backbone such as poly(methylmethacrylate) (PMMA) and polystyrene offer the possibility of achieving much lower TFT gate leakage current densities and greater environmental stability. These hydrophobic polymers are often soluble in common organic solvents but, because of the lack of crosslinking functionality, they cannot withstand subsequent solution-phase processing steps in which additional layers are deposited.

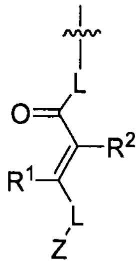
[0005] Accordingly, there is a desire in the art for crosslinkable polymeric dielectric materials that can exhibit low current leakage densities, that can be prepared via solution processes, that can be air- and/or moisture-stable, and that can be compatible with diverse gate and/or semiconductor materials.

Summary

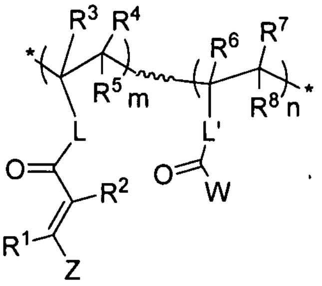
[0006] In light of the foregoing, the present teachings provide photopolymer-based dielectric materials (e.g. films) and associated devices that can address various deficiencies and shortcomings of the prior art, including those outlined above.

[0007] In one aspect, the present teachings provide photopolymers that can be used to prepare dielectric materials. Among other desirable properties, polymers of the present teachings can be soluble in common organic solvents but can become insoluble in the same solvents after undergoing crosslinking, for example, photocrosslinking, which gives rise to certain processing advantages. More specifically, the present teachings provide polymers having crosslinkable functional groups, for example, photocrosslinkable functional groups, that allow the polymers to crosslink. The crosslinking functionality can allow formation of a densely crosslinked polymeric matrix. Photopolymers of the present teachings and their crosslinked products can have excellent insulating properties, which enable their use as dielectrics. In some embodiments, the photopolymers and their crosslinked products can have a leakage current density that is less than or equals to about 1×10^{-8} A/cm^2 at 2 MV/cm.

[0008] Polymers of the present teachings can have a pendant group having the formula:



wherein R^1, R^2, L, and Z are as defined herein. In certain embodiments, the present teachings provide polymers having the formula:



wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, L, L', W, Z, m, and n are as defined herein.

[0009] The present teachings also provide dielectric materials that include the polymers described above. For example, the dielectric materials can be prepared from the polymers described above. Multilayer dielectric materials are provided which include two or more layers of dielectric materials sequentially deposited on top of each other, where at least one of the layers is prepared from polymers of the present teachings. These photopolymers can be used to prepare dielectric materials using various solution processes, including various printing techniques.

[0010] The present teachings further provide electronic devices that include or are made from any of the dielectric materials described above. Examples of electronic devices include, but are not limited to, organic thin film transistors (OTFTs) (e.g., organic field effect transistors (OFETs)) and capacitors. In addition to a dielectric component, these devices can include, for example, a substrate component, a semiconductor component, and/or a metallic contact component.

[0011] Methods for preparing the polymers, the dielectric materials, and the electronic devices described above are also provided and are within the scope of the present teachings.

[0012] The foregoing as well as other features and advantages of the present teachings will be more fully understood from the following figures, description, and claims.

Brief Description of the Drawings

[0013] It should be understood that the drawings described below are for illustration purposes only and are not necessarily to scale. The drawings are not intended to limit the scope of the present teachings in any way.

[0014] **Figure 1** provides leakage current density (J) versus electric field (E) plots of various metal-insulator-semiconductor capacitor structures of different feature sizes in which the insulating layer is a dielectric material of the present teachings [$P(CyVP_{0.55}\text{-co-}MMA_{0.45})$].

[0015] **Figure 2** provides leakage current density (J) versus electric field (E) plots of various metal-insulator-semiconductor capacitor structures that were fabricated using dielectric materials of the present teachings and other comparative dielectric materials.

[0016] **Figure 3** provides leakage current density (J) versus electric field (E) plots of various metal-insulator-semiconductor capacitor structures that were fabricated using dielectric materials of the present teachings and other comparative dielectric materials.

[0017] **Figure 4** provides representative transfer and output plots of pentacene-based organic field effect transistors fabricated with spin-coated dielectric materials of the present teachings [$P(CyEMA_{0.57}\text{-co-}F5BEMA_{0.43})$].

[0018] **Figure 5** provides representative transfer and output plots of n-type organic field effect transistors fabricated with spin-coated dielectric materials of the present teachings [$P(CyVP_{0.55}\text{-co-}MMA_{0.45})$].

[0019] **Figure 6** provides a leakage current density (J) versus electric field (E) plot of a metal-insulator-semiconductor capacitor structure that incorporates a two-layer dielectric material of the present teachings [P(CyVP$_{0.55}$-co-MMA$_{0.45}$)].

[0020] **Figure 7** provides representative transfer and output plots of a pentacene-based organic field effect transistor that incorporates a multilayer dielectric material of the present teachings [P(CyVP$_{0.55}$-co-MMA$_{0.45}$)].

[0021] **Figure 8** provides representative transfer and output plots of pentacene-based organic field effect transistors fabricated with printed dielectric materials of the present teachings [P(CyEMA$_{0.80}$-co-AcEMA$_{0.20}$)].

[0022] **Figure 9** shows an IR absorption spectrum of a dielectric material of the present teachings before and after crosslinking.

[0023] **Figure 10** shows a typical DSC plot of a polymer of the present teachings.

[0024] **Figure 11** shows a leakage current density (J) versus electric field (E) plot of a metal-insulator-semiconductor capacitor structure that incorporates a dielectric material of the present teachings having been stored in air for 55 days.

[0025] **Figure 12** provides representative transfer and output plots of an organic field effect transistor that incorporates a printed dielectric material of the present teachings and a drop-cast semiconductor layer prepared from N,N'-bis(n-octyl)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI-8CN$_2$).

[0026] **Figure 13** provides a leakage current density (J) versus electric field (E) plot of a metal-insulator-semiconductor capacitor structure that incorporates a dielectric material of the present teachings having a film thickness of 100 nm.

[0027] **Figure 14** provides leakage current density (J) versus electric field (E) plots of various metal-insulator-semiconductor capacitor structures that were fabricated using a dielectric material of the present teachings [P(CyVP$_{0.55}$-co-MMA$_{0.45}$)] and a comparative dielectric material [P(VP$_{0.30}$-co-CyVP$_{0.25}$-co-MMA$_{0.45}$)].

[0028] **Figure 15** provides leakage current density (J) versus electric field (E) plots of metal-insulator-semiconductor capacitor structures that were fabricated using spin-coated dielectric materials of the present teachings (photopatterned and rinsed versus no photopatterning/rinsing).

[0029] **Figure 16** illustrates different configurations of organic field effect transistors.

[0030] **Figure 17** provides representative transfer and output plots of a bottom-contact bottom-gate organic field effect transistor that incorporates a spin-coated dielectric material of the present teachings and a vapor-deposited semiconductor layer prepared from pentacene.

[0031] **Figure 18** provides a representative transfer plot of a bottom-contact top-gate organic field effect transistor that incorporates a spin-coated dielectric material of the present teachings and a vapor-deposited semiconductor layer prepared from pentacene.

[0032] **Figure 19** provides a representative output plot of a top-contact bottom-gate organic field effect transistor that incorporates a spin-coated dielectric material of the present teachings and a conducting polymer as the bottom-gate electrode.

Detailed Description

[0033] The present teachings relate to photopolymers that can be used to prepare dielectric materials, the dielectric materials so prepared, methods for preparing the photopolymers and the dielectric materials, as well as to compositions, articles, structures, and devices that include such photopolymers and dielectric materials.

[0034] More specifically, the present teachings provide solution-processable polymers that can be crosslinked, for example, photocrosslinked, to provide insoluble robust dielectric materials that can exhibit excellent insulating properties and can be used to fabricate various organic electronic devices, including OTFTs. The dielectric materials also can be air-stable and have long shelf stability, and can be compatible with a wide range of p-type and n-type organic and inorganic semiconductors, making them attractive materials for fabricating various organic electronic devices.

[0035] Throughout the description, where compositions are described as having, including, or comprising specific components, or where processes are described as having, including, or comprising specific process steps, it is contemplated that compositions of the present teachings also consist essentially of, or consist of, the recited components, and that the processes of the present teachings also consist essentially of, or consist of, the recited process steps.

[0036] In the application, where an element or component is said to be included in and/or selected from a list of recited elements or components, it should be understood that the element or component can be any one of the recited elements or components and can be selected from a group consisting of two or more of the recited elements or components. Further, it should be understood that elements and/or features of a composition, an apparatus, or a method described herein can be combined in a variety of ways without departing from the spirit and scope of the present teachings, whether explicit or implicit herein.

[0037] The use of the terms “include,” “includes,” “including,” “have,” “has,” or “having” should be generally understood as open-ended and non-limiting unless specifically stated otherwise.

[0038] The use of the singular herein includes the plural (and vice versa) unless specifically stated otherwise. In addition, where the use of the term “about” is before a quantitative value, the present teachings also include the specific quantitative value itself, unless specifically stated otherwise. As used herein, the term “about” refers to a ±10% variation from the nominal value.

[0039] It should be understood that the order of steps or order for performing certain actions is immaterial so long as the present teachings remain operable. Moreover, two or more steps or actions may be conducted simultaneously.

[0040] As used herein, “polymer” or “polymeric compound” refers to a molecule consisting of at least two repeating units (monomers) connected by covalent chemical bonds. The polymer or polymeric compound can have only one type of repeating unit as well as two or more types of different repeating units. In the latter case, the term “copolymer” or “copolymeric compound” can be used instead, especially when the polymer includes chemically significantly different repeating units. A polymer typically comprises a backbone with optional pendant groups. Unless specified otherwise, the assembly of the repeating units in the copolymer can be head-to-tail, head-to-head, or tail-to-tail. In addition, unless specified otherwise, the copolymer can be a random copolymer, an alternating copolymer, or a block copolymer. In some embodiments, formulae similar to the ones below can be used to represent a copolymer, and such formula should be interpreted to embrace a copolymer having any repeating pattern consisting of x % of Q^1, y % of Q^2, and z % of Q^3, where Q^1, Q^2, and Q^3 are different repeating units:

$$*\!-\!(Q^1)_x\!-\!(Q^2)_y\!-\!(Q^3)_z\!-\!* \quad \text{or} \quad *\!-\!(Q^1)_x\!\sim\!(Q^2)_y\!\sim\!(Q^3)_z\!-\!* .$$

[0041] As used herein, a “pendant group” refers to a moiety that is substituted on the backbone of a polymer.

[0042] As used herein, “photopolymer” refers to a polymer that can be cured, for example, crosslinked, by exposure to light, often in the ultraviolet region of the spectrum, or other types of radiation.

[0043] As used herein, “solution-processable” refers to compounds, materials, or compositions that can be used in various solution-phase processes including, but not limited to, spin-coating, printing (e.g., inkjet printing), spray coating, electrospray coating, drop casting, dip coating, and blade coating.

[0044] As used herein, “halo” or “halogen” refers to fluoro, chloro, bromo, and iodo.

[0045] As used herein, “amino” refers to $-NH_2$, an –NH–alkyl group, an $-N(alkyl)_2$ group, an –NH–arylalkyl group, an –N(alkyl)–arylalkyl group, and an $-N(arylalkyl)_2$ group, and is within the definition of $-NR^1R^2$, wherein R^1 and R^2 are as defined herein.

[0046] As used herein, “alkoxy” refers to –O–alkyl group, and is within the definition of

$-OR^3$, wherein R^3 is as defined herein. Examples of alkoxy groups include, but are not limited to, methoxy, ethoxy, propoxy (e.g., n-propoxy and isopropoxy), t-butoxy groups, and the like.

[0047] As used herein, “alkylthio” refers to an –S–alkyl group. Examples of alkylthio groups include, but are not limited to, methylthio, ethylthio, propylthio (*e.g.*, n-propylthio and isopropylthio), t-butylthio groups, and the like.

[0048] As used herein, “ester” refers to both an –O–C(O)–alkyl group and a –C(O)–O–alkyl group, where the former group is within the definition of $-OC(O)R^3$, and R^3 is as defined herein.

[0049] As used herein, “oxo” refers to a double-bonded oxygen (i.e., =O).

[0050] As used herein, “alkyl” refers to a straight-chain or branched saturated hydrocarbon group. Examples of alkyl groups include methyl (Me), ethyl (Et), propyl (e.g., n-propyl and isopropyl), butyl (e.g., n-butyl, isobutyl, sec-butyl, tert-butyl), pentyl groups (e.g., n-pentyl, isopentyl, neopentyl), and the like. In various embodiments, an alkyl group can have 1 to 30 carbon atoms, i.e., a C_{1-30} alkyl group, and, for example, an alkyl group can have 1 to 20 carbon atoms, i.e., a C_{1-20} alkyl group. In some embodiments, an alkyl group can have 1 to 6 carbon atoms, and can be referred to as a “lower alkyl group.” Examples of lower alkyl groups include methyl, ethyl, propyl (e.g., n-propyl and isopropyl), and butyl groups (e.g., n-butyl, isobutyl, sec-butyl, tert-butyl). In some embodiments, alkyl groups can be substituted as disclosed herein.

[0051] As used herein, "haloalkyl" refers to an alkyl group having one or more halogen substituents. Examples of haloalkyl groups include, but are not limited to, CF_3, C_2F_5, CHF_2, CH_2F, CCl_3, $CHCl_2$, CH_2Cl, C_2Cl_5, and the like. Perhaloalkyl groups, i.e., alkyl groups wherein all of the hydrogen atoms are replaced with halogen atoms (*e.g.*, CF_3 and C_2F_5), are included within the definition of "haloalkyl." For example, a C_{1-20} haloalkyl group can have the formula $-C_nX_{2n+1}$ or $-C_nH_{2n+1-t}X_t$, wherein X is F, Cl, Br, or I, n is an integer in the range of 1 to 20, and t is an integer in the range of 0 to 41, provided that t is less than or equal to 2n+1.

[0052] As used herein, "alkenyl" refers to a straight-chain or branched alkyl group having one or more carbon-carbon double bonds. Examples of alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, butadienyl, pentadienyl, hexadienyl groups, and the like. The one or more carbon-carbon double bonds can be internal (such as in 2-butene) or terminal (such as in 1-butene). In various embodiments, an alkenyl group can have 2 to 20 carbon atoms, i.e., a C_{2-20} alkenyl group. In some embodiments, alkenyl groups can be substituted as disclosed herein.

[0053] As used herein, "alkynyl" refers to a straight-chain or branched alkyl group having one or more triple carbon-carbon bonds. Examples of alkynyl groups include, but are not limited to, ethynyl, propynyl, butynyl, pentynyl, and the like. The one or more triple carbon-carbon bonds can be internal (such as in 2-butyne) or terminal (such as in 1-butyne). In various embodiments, an alkynyl group can have 2 to 20 carbon atoms, i.e., a C_{2-20} alkynyl group. In some embodiments, alkynyl groups can be substituted as disclosed herein.

[0054] As used herein, "cycloalkyl" refers to a non-aromatic carbocyclic group including cyclized alkyl, alkenyl, and alkynyl groups. A cycloalkyl group can be monocyclic (e.g., cyclohexyl) or polycyclic (e.g., containing fused, bridged, and/or spiro ring systems), wherein the carbon atoms are located inside or outside of the ring system. Any suitable ring position of the cycloalkyl group can be covalently linked to the defined chemical structure. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclopentenyl, cyclohexenyl, cyclohexadienyl, cycloheptatrienyl, norbornyl, norpinyl, norcaryl, adamantyl, and spiro[4.5]decanyl groups, as well as their homologs, isomers, and the like. In various embodiments, a cycloalkyl group can have 3 to 14 carbon atoms, including 3 to 10 carbon atoms (i.e., a C_{3-10} cycloalkyl group). In some embodiments, cycloalkyl groups can be substituted as disclosed herein.

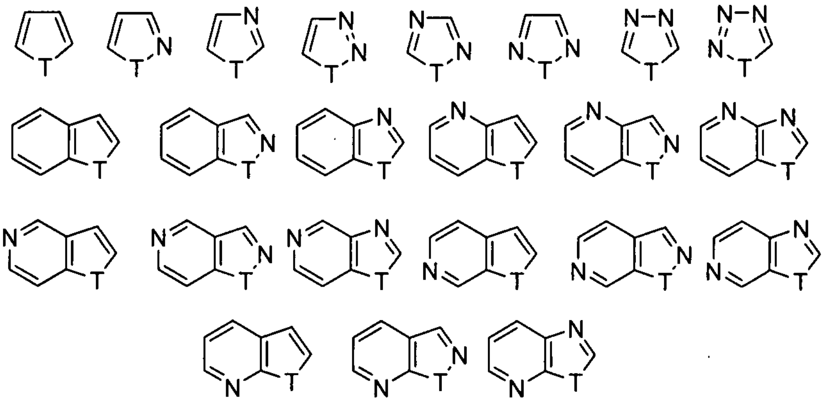
[0055] As used herein, “heteroatom” refers to an atom of any element other than carbon or hydrogen and includes, for example, nitrogen, oxygen, silicon, sulfur, phosphorus, and selenium.

[0056] As used herein, “cycloheteroalkyl” refers to a non-aromatic cycloalkyl group that contains at least one ring heteroatom selected from O, N, and S, and optionally contains one or more double or triple bonds. In various embodiments, a cycloheteroalkyl group can have 3 to 20 ring atoms, including 3 to 14 ring atoms (i.e., a 3-14 membered cycloheteroalkyl group). One or more N or S atoms in a cycloheteroalkyl ring may be oxidized (e.g., morpholine N-oxide, thiomorpholine S-oxide, thiomorpholine S,S-dioxide). In some embodiments, nitrogen atoms of cycloheteroalkyl groups can bear a substituent, for example, a hydrogen atom, an alkyl group, or other substituents as described herein. Cycloheteroalkyl groups can also contain one or more oxo groups, such as oxopiperidyl, oxooxazolidyl, dioxo-(1H,3H)-pyrimidyl, oxo-2(1H)-pyridyl, and the like. Examples of cycloheteroalkyl groups include, among others, morpholinyl, thiomorpholinyl, pyranyl, imidazolidinyl, imidazolinyl, oxazolidinyl, pyrazolidinyl, pyrazolinyl, pyrrolidinyl, pyrrolinyl, tetrahydrofuranyl, tetrahydrothiophenyl, piperidinyl, piperazinyl, and the like. In some embodiments, cycloheteroalkyl groups can be substituted as disclosed herein.

[0057] As used herein, “aryl” refers to an aromatic monocyclic hydrocarbon ring system or a polycyclic ring system in which two or more aromatic hydrocarbon rings are fused (i.e., having a bond in common with) together or at least one aromatic monocyclic hydrocarbon ring is fused to one or more cycloalkyl and/or cycloheteroalkyl rings. An aryl group can have from 6 to 14 carbon atoms in its ring system, which can include multiple fused rings. In some embodiments, a polycyclic aryl group can have from 7 to 14 carbon atoms. Any suitable ring position of the aryl group can be covalently linked to the defined chemical structure. Examples of aryl groups having only aromatic carbocyclic ring(s) include, but are not limited to, phenyl, 1-naphthyl (bicyclic), 2-naphthyl (bicyclic), anthracenyl (tricyclic), phenanthrenyl (tricyclic), and like groups. Examples of polycyclic ring systems in which at least one aromatic carbocyclic ring is fused to one or more cycloalkyl and/or cycloheteroalkyl rings include, among others, benzo derivatives of cyclopentane (i.e., an indanyl group, which is a 5,6-bicyclic cycloalkyl/aromatic ring system), cyclohexane (i.e., a tetrahydronaphthyl group, which is a 6,6-bicyclic cycloalkyl/aromatic ring system), imidazoline (i.e., a benzimidazolinyl group, which is a 5,6-bicyclic cycloheteroalkyl/aromatic ring system), and pyran (i.e., a chromenyl group, which is a 6,6-bicyclic cycloheteroalkyl/aromatic ring system). Other examples of aryl groups include, but are not limited to, benzodioxanyl, benzodioxolyl, chromanyl, indolinyl groups, and the like. In some embodiments, aryl groups can be substituted with up to five substitution groups as disclosed herein. For example, an aryl group can be substituted with one to five halogen substituents and such an aryl group can be referred to as a "haloaryl" group. An example of a haloaryl group is a perhalophenyl group, where the phenyl group is substituted with five halogen atoms.

[0058] As used herein, "heteroaryl" refers to an aromatic monocyclic ring system containing at least 1 ring heteroatom selected from oxygen (O), nitrogen (N), and sulfur (S) or a polycyclic ring system where at least one of the rings present in the ring system is aromatic and contains at least 1 ring heteroatom. Polycyclic heteroaryl groups include two or more heteroaryl rings fused together and monocyclic heteroaryl rings fused to one or more aromatic carbocyclic rings (aryl groups), non-aromatic carbocyclic rings (cycloalkyl groups), and/or non-aromatic cycloheteroalkyl groups. A heteroaryl group, as a whole, can have, for example, from 5 to 14 ring atoms and contain 1-5 ring heteroatoms. The heteroaryl group can be attached to the defined chemical structure at any heteroatom or carbon atom that results in a stable structure. Generally, heteroaryl rings do not contain O-O, S-S, or S-O bonds. However, one or more N or S atoms in a heteroaryl group can be oxidized (e.g., pyridine N-oxide, thiophene S-oxide, thiophene S,S-dioxide).

Examples of heteroaryl groups include, for example, the 5-membered monocyclic and 5-6 bicyclic ring systems shown below:



where T is O, S, NH, N-alkyl, N-aryl, or N-(arylalkyl) (e.g., N-benzyl). Examples of heteroaryl groups include pyrrolyl, furyl, thienyl, pyridyl, pyrimidyl, pyridazinyl, pyrazinyl, triazolyl, tetrazolyl, pyrazolyl, imidazolyl, isothiazolyl, thiazolyl, thiadiazolyl, isoxazolyl, oxazolyl, oxadiazolyl, indolyl, isoindolyl, benzofuryl, benzothienyl, quinolyl, 2-methylquinolyl, isoquinolyl, quinoxalyl, quinazolyl, benzotriazolyl, benzimidazolyl, benzothiazolyl, benzisothiazolyl, benzisoxazolyl, benzoxadiazolyl, benzoxazolyl, cinnolinyl, 1H-indazolyl, 2H-indazolyl, indolizinyl, isobenzofuyl, naphthyridinyl, phthalazinyl, pteridinyl, purinyl, oxazolopyridinyl, thiazolopyridinyl, imidazopyridinyl, furopyridinyl, thienopyridinyl, pyridopyrimidinyl, pyridopyrazinyl, pyridopyridazinyl, thienothiazolyl, thienoxazolyl, thienoimidazolyl, and the like. Further examples of heteroaryl groups include, but are not limited to, 4,5,6,7-tetrahydroindolyl, tetrahydroquinolyl, benzothienopyridyl, benzofuropyridyl, and the like. In some embodiments, heteroaryl groups can be substituted as disclosed herein.

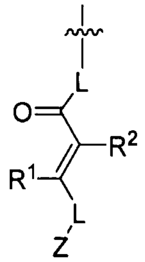
[0059] Compounds of the present teachings can include a "divalent group" defined herein as a linking group capable of forming a covalent bond with two other moieties. For example, compounds of the present teachings can include, but are not limited to, a divalent C_{1-20} alkyl group such as a methylene group.

[0060] As used herein, a "leaving group" ("LG") refers to a charged or uncharged atom (or group of atoms) that can be displaced as a stable species as a result of, for example, a substitution or elimination reaction. Examples of leaving groups include, but are not limited to, halide (e.g., Cl, Br, I), tosylate (toluenesulfonyl group, TsO), mesylate (methanesulfonyl group, MsO), brosylate (p-bromobenzenesulfonyl group, BsO), nosylate (4-nitrobenzenesulfonyl group, NsO), water (H_2O), ammonia (NH_3), and triflate (trifluoromethanesulfonyl group, OTf).

[0061] At various places in the present specification, substituents of compounds are disclosed in groups or in ranges. It is specifically intended that the description include each and every individual subcombination of the members of such groups and ranges. For example, the term "C_{1-6} alkyl" is specifically intended to individually disclose C_1, C_2, C_3, C_4, C_5, C_6, C_1-C_6, C_1-C_5, C_1-C_4, C_1-C_3, C_1-C_2, C_2-C_6, C_2-C_5, C_2-C_4, C_2-C_3, C_3-C_6, C_3-C_5, C_3-C_4, C_4-C_6, C_4-C_5, and C_5-C_6 alkyl. By way of other examples, an integer in the range of 0 to 40 is specifically intended to individually disclose 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, and 40, and an integer in the range of 1 to 20 is specifically intended to individually disclose 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, and 20.

[0062] Throughout the specification, structures may or may not be presented with chemical names. Where any question arises as to nomenclature, the structure prevails.

[0063] In one aspect, the present teachings provide photopolymers that include one or more crosslinkable functionalities. The crosslinking group can form or be a portion of a pendant group covalently attached to the backbone of the polymers. More specifically, the present teachings provide a polymer including a pendant group having the formula:



wherein:

L, at each occurrence, is independently –Y–, –Y–O–Y–, –Q–, –Y–S–Y–, –Y–C(O)–O–Y–, –Q–C(O)–O–Y–, –Y–O–C(O)–Q–, –Y–O–C(O)–Y–, –Q–C(O)–Q–, –Y–C(O)–Y–, –Q–C(O)–Y–, or –Y–C(O)–Q–;

wherein:

Q, at each occurrence, is $-O-[Y-O]_p-Y-O-$;

Y, at each occurrence, is a divalent C_{1-10} alkyl group, a divalent C_{2-10} alkenyl group, a divalent C_{2-10} alkynyl group, a divalent C_{6-10} aryl group, or a covalent bond, wherein each of the C_{1-10} alkyl group, the C_{2-10} alkenyl group, the C_{2-10} alkynyl group, and the C_{6-10} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN; and

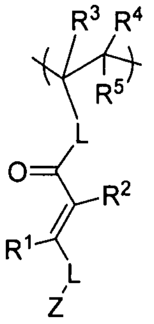
p is an integer in the range of 0 to 10;

R^1 and R^2 are independently H, a halogen, or CN; and

Z is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-20} alkyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, a $-O-C_{1-20}$ haloalkyl group, a $-C(O)-C_{1-6}$ alkyl group, a $-C(O)-C_{1-6}$ haloalkyl group, and a $-C(O)-O-C_{1-6}$ alkyl group.

[0064] In some embodiments, R^1 and R^2 can be independently H or F. In certain embodiments, Z can be a C_{1-6} alkyl group, a C_{1-6} perfluoroalkyl group, or a phenyl group optionally substituted with 1 to 5 substituents independently selected from a halogen such as F, a C_{1-20} alkyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, and a $-O-C_{1-20}$ haloalkyl group. For example, Z can be a phenyl group, a perhalophenyl group, or a phenyl group substituted with a trifluoromethyl group, a C_{1-20} alkoxy group, or a $-O-C_{1-20}$ haloalkyl group. In some embodiments, L, at each occurrence, can be independently –O–, $-C_6H_5-O-$, –C(O)–O–, $-C(O)-O-CH_2CH_2-O-$, $-C(O)-O-CF_2CF_2-O-$, or a covalent bond.

[0065] In various embodiments, polymers of the present teachings can have a repeating unit having the formula:

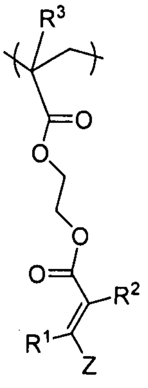


wherein:

R^3, R^4, and R^5 are independently H, a halogen, a C_{1-10} alkyl group, or a C_{6-14} aryl group, wherein each of the C_{1-10} alkyl group and the C_{6-14} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN; and

R^1, R^2, L, and Z are as defined herein.

[0066] In some embodiments, polymers of the present teachings can have a repeating unit having a formula selected from:



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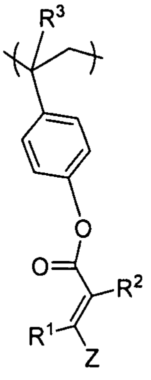

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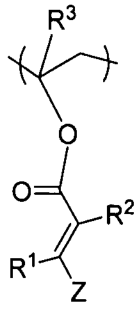

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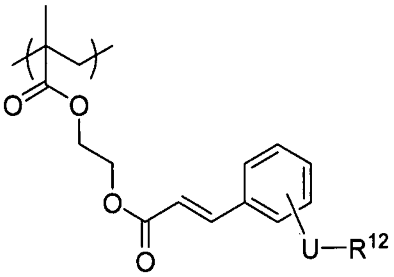
wherein R^1, R^2, R^3, and Z are as defined herein. For example, polymers of the present teachings can have a repeating unit having the formula:



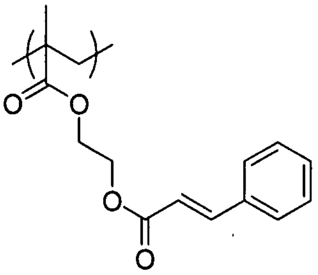
wherein:

U is –Y– or –Y–O–Y–;

R^{12} is H, a $C_{1\text{-}20}$ alkyl group, or a $C_{1\text{-}20}$ haloalkyl group; and

Y is as defined herein.

[0067] In some embodiments, U can be –O– or a covalent bond. In some embodiments, R^{12} can be H, $-CF_3$, a hexyl group, a decyl group, an octadecyl group, or $-(CH_2)_3(CF_2)_7CF_3$. For example, polymers of the present teachings can have a repeating unit selected from:



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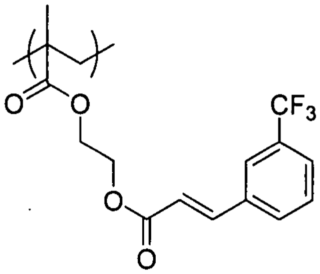

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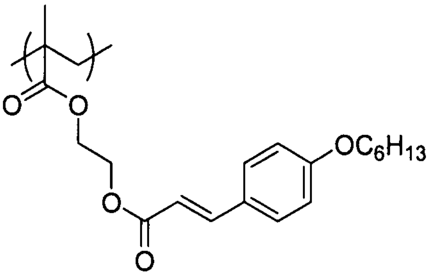

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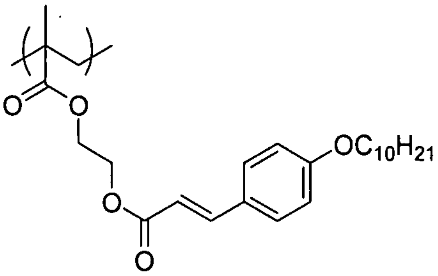

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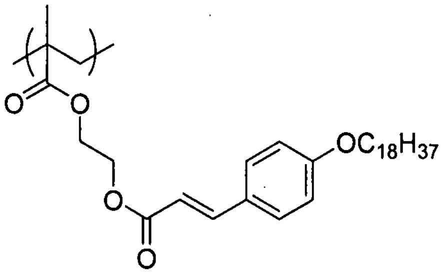

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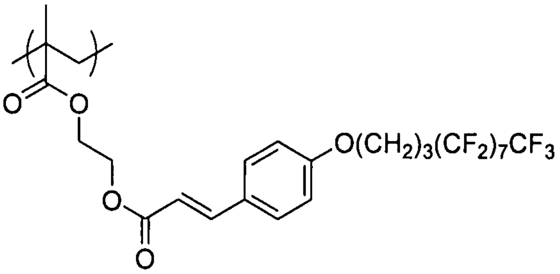

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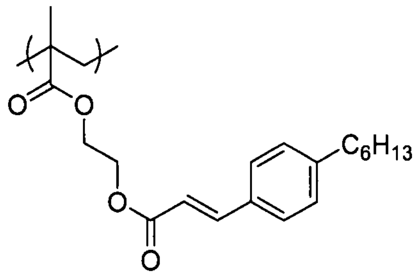

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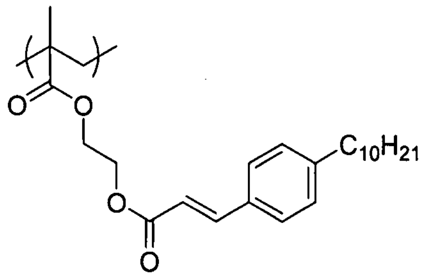

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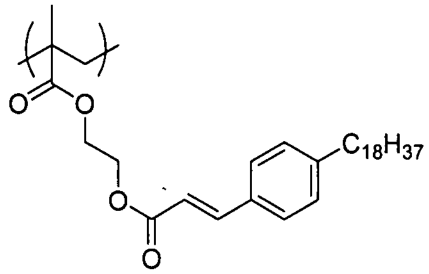

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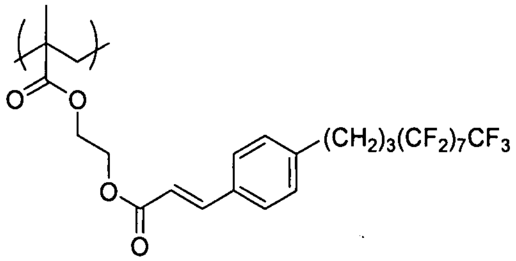
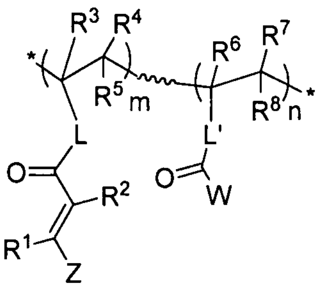


.

[0068] In various embodiments, polymers of the present teachings can have the formula:



,

wherein:

R^6, R^7, and R^8 are independently H, a halogen, a C_{1-10} alkyl group, or a C_{6-14} aryl group, wherein each of the C_{1-10} alkyl group and the C_{6-14} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN;

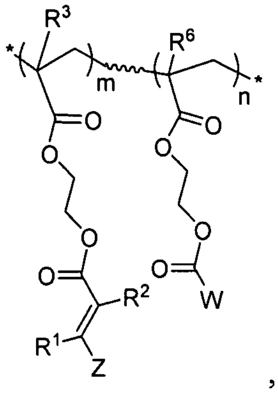
L' is –Y–, –Y–O–Y–, –Q–, –Y–S–Y–, –Y–C(O)–O–Y–, –Q–C(O)–O–Y–, –Y–O–C(O)–Q–, –Y–O–C(O)–Y–, –Q–C(O)–Q–, –Y–C(O)–Y–, –Q–C(O)–Y–, or –Y–C(O)–Q–;

W is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, a C_{1-10} alkoxy group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{1-6} alkoxy group, a –C(O)–C_{1-6} alkyl group, a –C(O)–C_{1-6} haloalkyl group, and a –C(O)–O–C_{1-6} alkyl group;

m and n are independently a real number, wherein $0 < m \leq 1$, $0 \leq n < 1$, and $m + n = 1$; and

R^1, R^2, R^3, R^4, R^5, L, Q, Y, and Z are as defined herein.

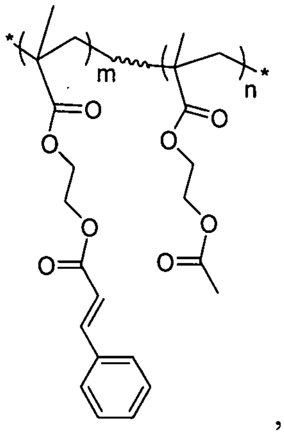
[0069] In some embodiments, the polymers can have the formula:



,

wherein R^1, R^2, R^3, R^6, W, Z, m, and n are as defined herein.

[0070] For example, the polymers can have a formula selected from:



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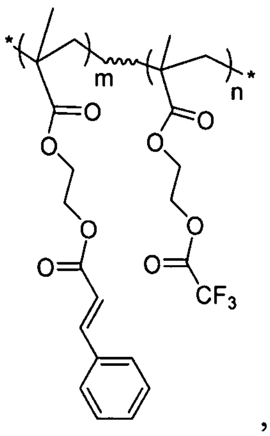

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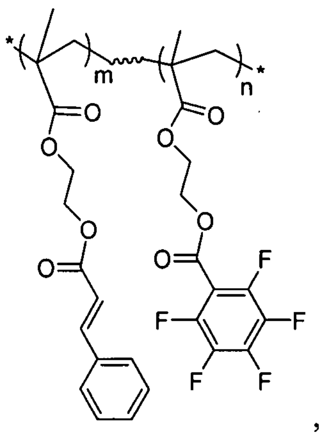

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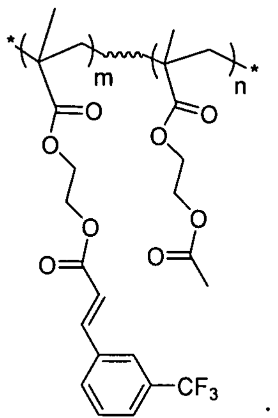
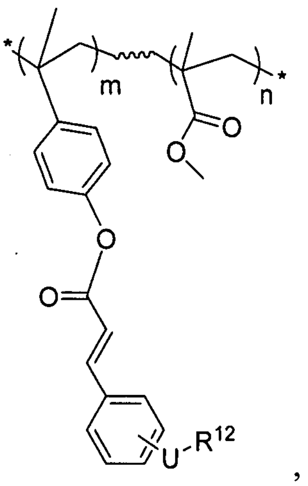


;

wherein m and n are as defined herein.

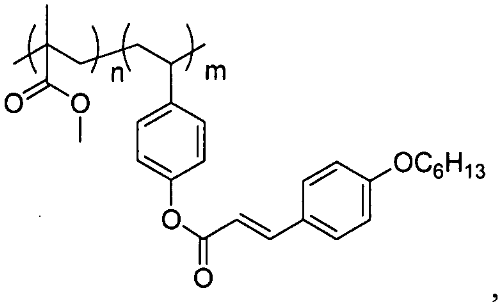
[0071] In some embodiments, the polymer can have the formula:



,

wherein m, n, R^{12}, and U are as defined herein.

[0072] For example, the polymer can have a formula selected from:



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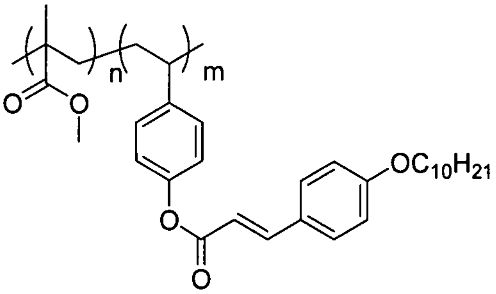

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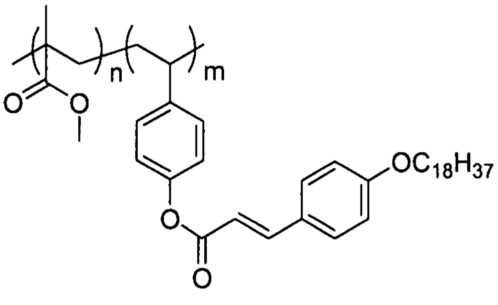

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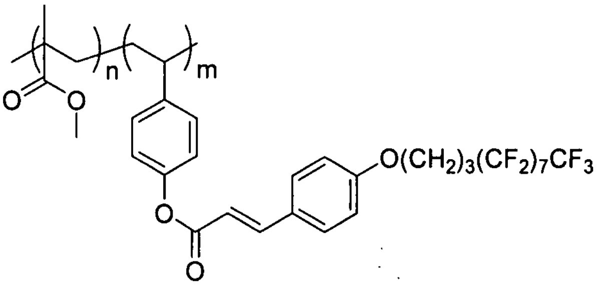

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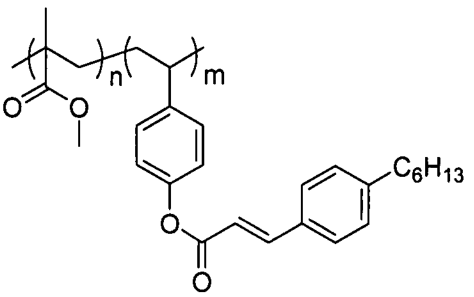

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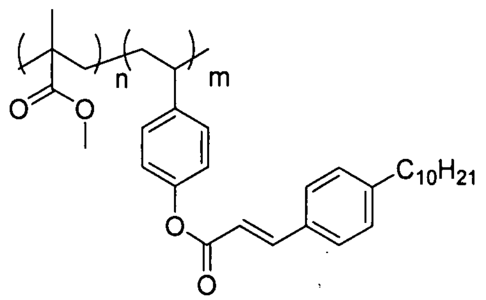

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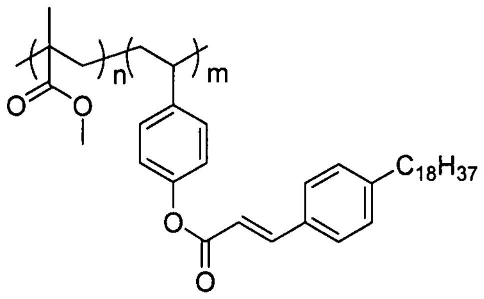

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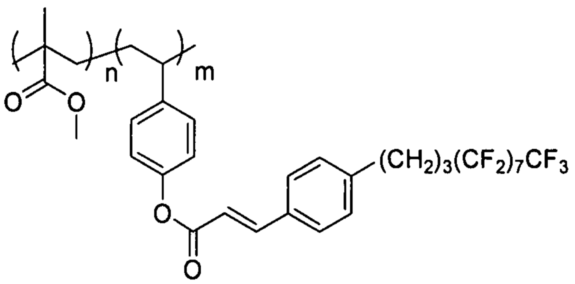
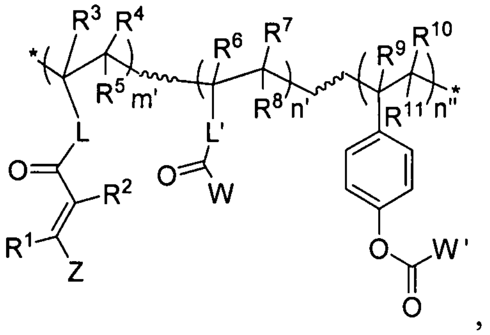


;

wherein m and n are as defined herein.

[0073] In some embodiments, the polymer can have the formula:



,

wherein:

R^9, R^{10}, and R^{11} are independently H, a halogen, a C_{1-10} alkyl group, or a C_{6-14} aryl group, wherein each of the C_{1-10} alkyl group and the C_{6-14} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN;

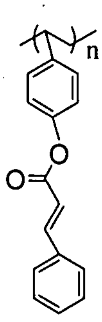
W' is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, a C_{1-10} alkoxy group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{1-6} alkoxy group, a $-C(O)-C_{1-6}$ alkyl group, a $-C(O)-C_{1-6}$ haloalkyl group, and a $-C(O)-O-C_{1-6}$ alkyl group;

m', n', and n" are independently a real number, wherein $0 < m' \leq 1$, $0 \leq n' < 1$, $0 \leq n'' < 1$, and $m' + n' + n'' = 1$; and

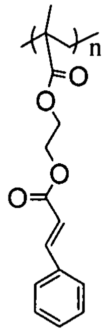
R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, L, L', W, and Z are as defined herein.

[0074] In certain embodiments, W' can be a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{1-6} alkoxy group, a –C(O)–C_{1-6} alkyl group, a –C(O)–C_{1-6} haloalkyl group, and a –C(O)–O–C_{1-6} alkyl group. For example, W' can be a C_{1-6} alkyl group or a C_{1-6} haloalkyl group. In particular embodiments, W' can be CF_3.

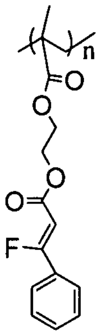
[0075] Polymers of the present teachings can include, but are not limited to, the polymers below:



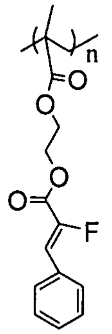
PCyVP



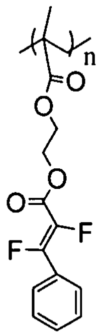
PCyEMA



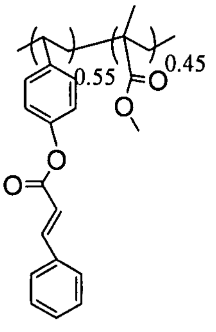
P3FCyEMA



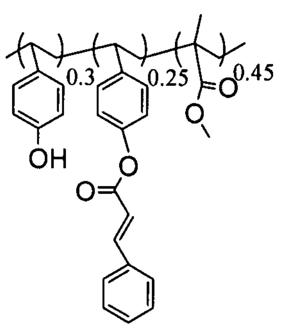
P2FCyEMA



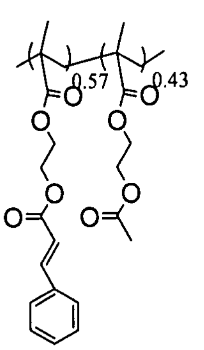
PF$_2$CyEMA



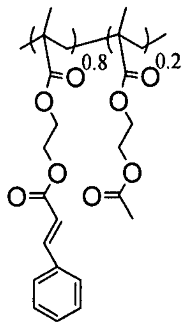
P(CyVP$_{0.55}$-*co*-MMA$_{0.45}$)



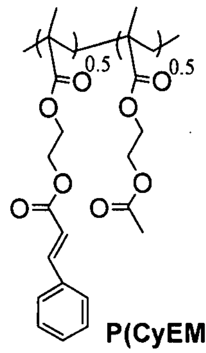
P(VP$_{0.3}$-*co*-CyVP$_{0.25}$-*co*-MMA$_{0.45}$)



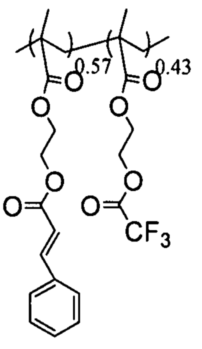
P(CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)



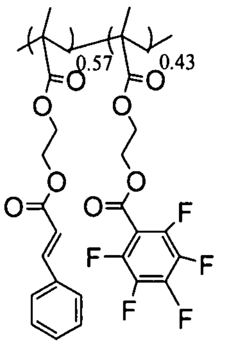
P(CyEMA$_{0.80}$-*co*-AcEMA$_{0.20}$)



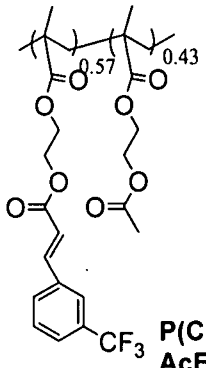
P(CyEMA$_{0.50}$-*co*-AcEMA$_{0.50}$)



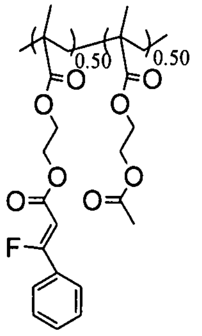
P(CyEMA$_{0.57}$-*co*-TFAcEMA$_{0.43}$)



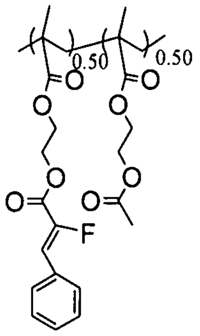
P(CyEMA$_{0.57}$-*co*-F5BEMA$_{0.43}$)



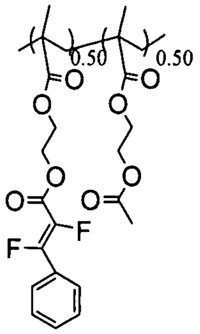
P(CF3CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)



P(3FCyEMA$_{0.50}$-*co*-AcEMA$_{0.5}$



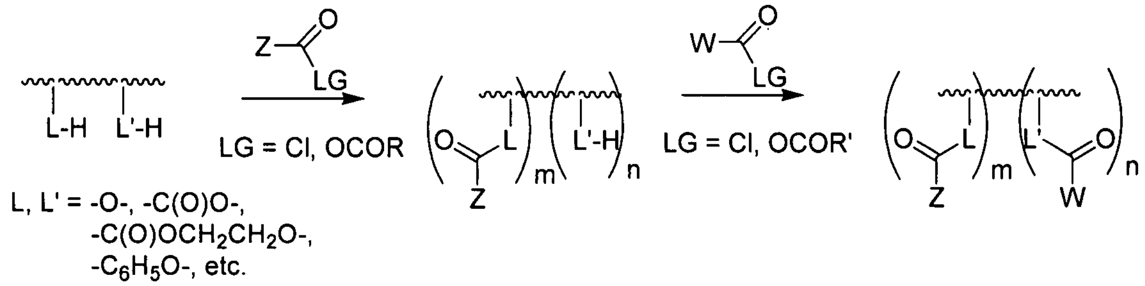
P(2FCyEMA$_{0.50}$-*co*-AcEMA$_{0.5}$



P(F2CyEMA$_{0.50}$-*co*-AcEMA$_{0.5}$

[0076] Photopolymers of the present teachings can be synthesized following Scheme 1 below. Other synthetic routes, including known to those skilled in the art, also can be used.

Scheme 1



[0077] In the scheme above, the desired pendant group can be coupled to a polymer, for example, a hydrophobic polymeric backbone, by reacting nucleophilic groups on the polymer with an acyl chloride, an acyl anhydride, or similar derivatives and groups that can form covalent bonds with nucleophilic groups, for example, electrophilic groups. Without wishing to be bound to any particular theory, it is believed that by derivatizing the OH groups of the polymer to other less acidic groups, polymers of the present teachings can have lower current leakages, as well as improved shelf stability. In some embodiments,

[0078] The polymers disclosed herein can have satisfactory solubility in common organic solvents. Examples of common organic solvents include, but are not limited to, petroleum ethers; aromatic hydrocarbons such as benzene, chlorobenzene, dichlorobenzene, cyclohexylbenzene, toluene, xylene, and mesitylene; ketones such as acetone, 2-butanone, and cyclohexanone; ethers such as tetrahydrofuran, diethyl ether, bis(2-methoxyethyl) ether, and dioxane; alcohols such as ethanol, propanol, and isopropyl alcohol; aliphatic hydrocarbons, such as hexanes; acetates, such as ethyl acetate; halogenated aliphatic hydrocarbons such as dichloromethane, chloroform, and ethylene chloride; and other aprotic solvents such as dimethyl formamide and n-methyl pyrrolidone. As used herein, a compound can be considered soluble in a solvent when at least 1 mg of the compound can be dissolved in 1 mL of the solvent.

[0079] Polymers of the present teachings can be used in various solution-phase processes including, but not limited to, spin-coating, printing, drop casting, dip coating, spraying, and blade coating. Spin-coating involves applying an excess amount of the coating solution onto a substrate, then rotating the substrate at high speed to spread the fluid by centrifugal force. The thickness of the resulting dielectric film prepared by this technique is dependent on the spin-coating rate, the concentration of the solution, as well as the solvent used. Printing can be performed, for example, with a rotogravure printing press, a flexo printing press, or an inkjet printer. The thickness of the dielectric film in these cases will similarly be dependent on the concentration of the solution, the choice of solvent, and the number of printing repetitions. Ambient conditions such as temperature, pressure, and humidity, can also affect the resulting thickness of the film. Depending on the specific printing techniques used, printing quality can be affected by different parameters including, but not limited to, rheological properties of the inks such as solubility and viscosity. For noncontact printing techniques such as inkjet printing, the solubility requirement is generally less stringent and a solubility range as low as about 1-4 mg/mL can suffice. For gravure printing, a higher solubility range may be necessary, often in the range of about 50-100 mg/mL. Other contact printing techniques such as screen-printing and flexo printing, can require even higher solubility ranges, for example, about 100-1000 mg/mL.

[0080] One of the advantages of the polymers disclosed herein is their ability to crosslink, for example, photocrosslink, after deposition onto a substrate. The crosslinking functionality allows formation of a densely crosslinked polymeric matrix. The crosslinked polymeric matrix is robust enough to withstand various conditions that are common in device fabrication processes, including patterning and subsequent solution-phase processes, for example, to form/deposit overlying layers (e.g., the semiconductor layer in a top-contact OFET). Without wishing to be bound to any particular theory, the crosslinking chemistry can include a 2+2 photo-stimulated cycloaddition that provides stable cyclobutane moieties. The crosslinking chemistry can also involve free radical additions. Polymers of the present teachings can be cured, for example, photocrosslinked, by exposure to ultraviolet light at, for example, a wavelength of about 245 nm to 350 nm. Crosslinking can also be achieved by other types of radiation, for example, with ion beams of charged particles, and with radioactive sources. Subsequent to the formation of the crosslinked matrix, the dielectric material of the present teachings can be subject to further patterning and process steps, by which additional layers, including additional dielectric, semiconductor and/or conducting layers, can be formed on top of the dielectric material.

[0081] Photopolymers of the present teachings can be used to prepare dielectric materials that can exhibit a wide range of desirable properties and characteristics including, but not limited to, low leakage current densities, high breakdown voltages, low hysteresis, large capacitance, uniform film thickness, solution-processability, fabricability at low temperatures and/or atmospheric pressures, air and moisture stability, and/or compatibility with diverse gate materials and/or semiconductors.

[0082] Leakage current density is typically defined as a vector whose magnitude is the leakage current per cross-sectional area. As used herein, “leakage current” refers to uncontrolled (“parasitic”) current flowing across region(s) of a semiconductor structure or device in which no current should be flowing, for example, current flowing across the gate oxide in a metal-oxide-semiconductor (MOS) structure. As known by those skilled in the art, the leakage current density of a dielectric material can be determined by fabricating a standard metal-insulator-semiconductor (MIS) and/or metal-insulator-metal (MIM) capacitor structures with the dielectric material, then measuring the leakage current, and dividing the measured current by the area of the metal electrodes.

[0083] Photopolymers of the present teachings and their crosslinked products can have very low leakage current densities as measured from standard MIS and MIM capacitor structures. For example, photopolymers of the present teachings and their crosslinked products can have a leakage current density of less than or equal to about 4×10^{-8} A/cm^2 at 2 MV/cm, less than or equal to about 2×10^{-8} A/cm^2 at 2 MV/cm, less than or equal to about 1×10^{-8} A/cm^2 at 2 MV/cm, less than or equal to about 8×10^{-9} A/cm^2 at 2 MV/cm, less than or equal to about 7×10^{-9} A/cm^2 at 2 MV/cm, less than or equal to about 6×10^{-9} A/cm^2 at 2 MV/cm, less than or equal to about 4×10^{-9} A/cm^2 at 2 MV/cm, less than or equal to about 2×10^{-9} A/cm^2 at 2 MV/cm, or less than or equal to about 1×10^{-9} A/cm^2 at 2 MV/cm. Photopolymers of the present teachings also exhibit low leakage current densities at higher voltages, for example, a leakage current density of less than or equal to about 1×10^{-6} A/cm^2

at 4 MV/cm, less than or equal to about 5 x 10^{-7} A/cm^2 at 4 MV/cm, less than or equal to about 3 x 10^{-7} A/cm^2 at 4 MV/cm, less than or equal to about 1 x 10^{-7} A/cm^2 at 4 MV/cm, less than or equal to about 5 x 10^{-8} A/cm^2 at 4 MV/cm, or less than or equal to about 1 x 10^{-8} A/cm^2 at 4 MV/cm.

[0084] Dielectric materials prepared from photopolymers of the present teachings also were found to be able to withstand very high breakdown voltages (i.e., the maximum voltage difference that can be applied across the dielectric before it breaks down and begins to conduct). For example, dielectric materials of the present teachings can withstand a breakdown voltage of 4 MV/cm or higher, a breakdown voltage of 6 MV/cm or higher, or a breakdown voltage of 7 MV/cm or higher.

[0085] Polymers of the present teachings also can have relatively low glass transition temperatures. For example, polymers of the present teachings can have a glass transition temperature of less than about 100°C, a glass transition temperatures of less than about 90°C, a glass transition temperatures of less than about 80°C, a glass transition temperatures of less than about 70°C, a glass transition temperatures of less than about 60°C, a glass transition temperatures of less than about 50°C, a glass transition temperatures of less than about 40°C, or a glass transition temperatures of less than about 30°C. In particular embodiments, polymers of the present teachings can have a glass transition temperature in the range of about 30°C to about 60°C. Glass transition temperature (T_g) can be defined as the mid-point of a temperature range at which a material gradually becomes more viscous and changes from a rubbery state to a glassy state. Due to this property, dielectric materials deposited from polymers of the present teachings can allow surface planarization and filling of pinholes before crosslinking, hence improving surface smoothness (for example, achieving a sub-nanometer surface roughness), and accordingly, device performance and operation. Pinholes can also be filled by depositing two or more layers of dielectric materials sequentially on top of one another, hence forming a multilayer dielectric material that can have very good surface uniformity and can be essentially pinhole-free over a large area.

[0086] The present teachings further provide articles of manufacture, for example, composites, that includes a dielectric material of the present teachings and a substrate component and/or a semiconductor component. The substrate component can be selected from, but is not limited to, doped silicon, an indium tin oxide (ITO), ITO-coated glass, ITO-coated polyimide or other plastics, aluminum or other metals alone or coated on a polymer or other substrate, a doped polythiophene, and the like. The composite can include a semiconductor component. The semiconductor component can be selected from, but is not limited to, various fused heterocycles, polythiophenes, fused aromatics, and other such organic semiconductor compounds or materials, whether p-type or n-type, otherwise known or found useful in the art. The semiconductor component also can include inorganic semiconductor materials such as silicon, germanium, gallium arsenide, and the like. The composite can include one or more electrical contacts. Such electrical contacts can be made of a metal (e.g., gold) and can function as source, drain, or gate contacts. One or more of the composites described above can be embodied within various organic electronic devices such as OTFTs, specifically, OFETs, as well as capacitors, complementary circuits (e.g., inverter circuits), and the like.

[0087] Another aspect of the present teachings relates to methods for preparing a dielectric material. The method can include preparing a solution that includes the polymer described herein, and printing the solution onto a substrate to form a dielectric layer. The method can include exposing the dielectric layer to a radiation source (e.g., ultraviolet light) to induce crosslinking, thereby forming a crosslinked dielectric material. The method can also include printing an additional dielectric layer onto the crosslinked dielectric layer to form a multilayer dielectric material.

[0088] Another aspect of the present teachings relates to methods for fabricating organic field effect transistors that include a dielectric material of the present teachings. The dielectric materials of the present teachings can be used to fabricate various types of organic field effect transistors including, but not limited to, top-gate top-contact capacitor structures, top-gate bottom-contact capacitor structures, bottom-gate top-contact capacitor structures, and bottom-gate bottom-contact capacitor structures.

[0089] In some embodiments, the method can include preparing a solution that includes the polymer described herein, printing the solution onto a substrate (gate) to form a dielectric layer, exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material, forming a semiconductor layer on the crosslinked dielectric material, and forming a first electrical contact and a second electrical contact (source and drain) on the semiconductor layer, to fabricate a top-contact bottom-gate organic field effect transistor.

[0090] In other embodiments, the method can include preparing a solution that includes one or more polymers described herein, printing the solution onto a substrate (gate) to form a dielectric layer, exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material, forming a first electrical contact and a second electrical contact (source and drain) on the crosslinked dielectric material, and forming a semiconductor layer above the first and second electrical contacts and the dielectric material (i.e., to cover the electrical contacts and an area of the dielectric material between the electrical contacts), to fabricate a bottom-contact bottom-gate organic field effect transistor.

[0091] In some embodiments, the method can include forming a first electrical contact and a second electrical contact (source and drain) on a substrate, forming a semiconductor layer above the substrate and the first and second electrical contacts (to cover the electrical contacts and an area of the substrate between the electrical contacts), preparing a solution that includes one or more polymers described herein, printing the solution onto the semiconductor layer to form a dielectric layer, exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material, forming a third electrical contact (gate) on the crosslinked dielectric material, wherein the third electrical contact is above an area between the first and second electrical contacts, to fabricate a bottom-contact top-gate organic field effect transistor.

[0092] In other embodiments, the method can include forming a semiconductor layer on a substrate, forming a first electrical contact and a second electrical contact (source and drain) on the semiconductor layer, preparing a solution that includes one or more polymers described herein, printing the solution onto the first and second electrical contacts and an area of the semiconductor layer between the first and second electrical contacts to form a dielectric layer, exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material, and forming a third electrical contact (gate) on the dielectric material, wherein the third electrical contact is above an area between the first and second electrical contacts, to fabricate a top-contact top-gate organic field effect transistor.

[0093] The semiconductor layer and the various electrical contacts can be formed by various deposition processes known to those skilled in the art. For example, the semiconductor layer can be formed by processes such as, but not limited to, physical vapor deposition, different types of printing techniques (e.g., flexo printing, litho printing, gravure printing, ink-jetting, pad printing, and so forth), drop casting, dip coating, doctor blading, roll coating, and spin-coating. Electrical contacts can be formed by processes such as, but not limited to, thermal evaporation and radiofrequency or e-beam sputtering, as well as various deposition processes, including but not limited to those described immediately above (e.g., flexo printing, litho printing, gravure printing, ink-jetting, pad printing, drop casting, dip coating, doctor blading, roll coating, and spin-coating).

[0094] In the following examples, polymers and dielectric materials according to the present teachings were prepared and characterized by NMR, IR spectroscopy, elemental analysis, differential scanning calorimetry (DSC), AFM, and metal-insulator-semiconductor (MIS) device leakage and impedance spectroscopy measurements, to demonstrate, among other things, their dielectric properties and their compatibility with various p-type and n-type organic semiconductors. Organic electronic devices, for example, organic thin film transistors (OTFTs), specifically, organic field effect transistors (OFETs), based on these dielectric films also have been fabricated and characterized, data of which are provided below.

[0095] The following examples are provided to illustrate further and to facilitate the understanding of the present teachings and are not in any way intended to limit the invention.

Example 1: Preparation of poly(vinylphenylcinnamate) (PCyVP)

[0096] Poly(vinylphenol) (2.0 g, $M_w = 20{,}000$ g/mol) was dissolved in 20 mL of anhydrous tetrahydrofuran (THF), to which 5 mL of anhydrous triethylamine (excess) was added. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (5.25 g, excess) in 5 mL of anhydrous THF. After stirring overnight, the reaction mixture was filtered and the polymer precipitates were purified by repetitive precipitation to yield about 2.5 g of poly(vinylphenylcinnamate) (PCyVP) as a white powder.

[0097] ^{1}H NMR (500Mz, $CDCl_3$): δ 6.58-7.81 (m, 11H, aromatic and allyl protons), 0.6-1.8 (m, 3H, alkyl protons).

Example 2: Preparation of poly(cinnamoylethylmethacrylate) [P(CyEMA)]

[0098] Poly(hydroxyethyl methacrylate) (2.0 g, $M_w = 20{,}000$ g/mol, hydroxyl group: 15.4 mmol) was dissolved in 20 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (6 g, 36 mmol) in 6 mL of anhydrous THF. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold methanol (MeOH). The polymer precipitates were purified by repetitive precipitation to yield about 2.5 g of poly(cinnamoylethylmethacrylate) [P(CyEMA)] as a white solid.

[0099] ^{1}H NMR (500Mz, $CDCl_3$): δ 7.65(d, 1H, -CH=CH-), 7.51(s, broad, 2H, aromatic), 7.33(s, broad, 3H, aromatic), 6.45(d, 1H, -CH=CH-), 4.09-4.28(m, 4H, OCH_2CH_2O), 2.06(s, sharp, 3H, OCH_3), 1.84-0.96 (m, 5H, CCH_3, $-CH_2-$).

Example 3: Preparation of random copolymer poly(vinylcinnamate-*co*-methylmethacrylate) [P($CyVP_{0.55}$-co-$MMA_{0.45}$)]

[0100] Poly(vinylphenol-co-methyl methacrylate) (10.0 g, $M_w = 8{,}000$ g/mol, hydroxyl group: 50 mmol, vinylphenol moiety molar ratio 55% based on calculation from proton NMR intergrations) was dissolved in 80 mL of anhydrous THF, to which 9.6 mL of anhydrous triethylamine was added. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (10.95 g, 66 mmol) in 30 mL of anhydrous THF. The reaction was heated to 50°C and stirred overnight, after which the reaction mixture was precipitated in 700 mL of cold MeOH. The precipitate was filtered, washed with MeOH, re-dissolved in 100 mL of THF, and precipitated again. After further precipitation (three times in total), over 11 g of random copolymer poly(vinylcinnamate-*co*-methylmethacrylate) [P(CyVP$_{0.55}$-*co*-MMA$_{0.45}$)] were obtained as a white powder.

[0101] ^{1}H NMR verified the copolymer ratio of cinnamoyl moiety and methacrylate moieties as 55%:45%. ^{1}H NMR (500Mz, $CDCl_3$): δ 6.63-7.84 (m, 11H, aromatic, -CH=CH-), 0.70-3.63 (m, 13H, alkyl protons). Elemental analysis, found: C, 76.31%, H, 6.31%; calculated: C, 76.27%, H, 6.19%.

Example 4 (comparative example): Preparation of random copolymer poly(vinylphenol-*co*-vinyl cinnamate-*co*-methylmethacrylate) [P(VP$_{0.30}$-*co*-CyVP$_{0.25}$-*co*-MMA$_{0.45}$)]

[0102] Poly(vinylphenol-co-methyl methacrylate) (8.0 g, M_w = 8,000 g/mol, hydroxyl group: 40 mmol, vinylphenol moiety molar ratio 55% based on calculation from proton NMR intergrations) was dissolved in 60 mL of anhydrous THF, to which 2.6 mL of anhydrous triethylamine was added. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (3 g, 18 mmol) in 20 mL of anhydrous THF. The solution was heated to 50°C and stirred overnight, after which the reaction mixture was filtered. The clear solution was placed under vacuum to remove triethylamine and the solvent to give 8 g of a random copolymer poly(vinylphenol-*co*-vinyl cinnamate-*co*-methylmethacrylate) [P(VP$_{0.30}$-*co*-CyVP$_{0.25}$-*co*-MMA$_{0.45}$)] as a pale yellow polymer.

[0103] ^{1}H NMR verified the copolymer ratio of phenol, cinnamoyl and methacrylate moieties as 30%, 25%, and 45%. ^{1}H NMR (500Mz, dioxane-d8): δ 6.48-7.82 (m, 11H, aromatic, -CH=CH-), 0.64-2.98 (m, 8H, alkyl protons).

Example 5: Preparation of high molecular weight random copolymer poly(cinnamoylethyl methacrylate-co-acetoxyethyl methacrylate) [P(CyEMA$_{0.50}$-*co*-AcEMA$_{0.50}$)]

[0104] Poly(hydroxyethyl methacrylate) (2.0 g, M_w = 1,000,000 g/mol, hydroxyl group: 15.4 mmol) was dissolved in 60 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (1.28 g, 7.7 mmol) in 4 mL of anhydrous THF. The reaction was stirred at room temperature for 30 minutes, after which 3 mL of acetic anhydride (excess) were added to cap the free OH groups on the polymer. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold MeOH. The polymer precipitates were purified by repetitive precipitation to give about 2 g of a high molecular weight random copolymer poly(cinnamoylethyl methacrylate-co-acetoxyethyl methacrylate) [P(CyEMA$_{0.50}$-*co*-AcEMA$_{0.50}$)] as a white solid.

[0105] ^{1}H NMR verified the copolymer ratio as 50%:50%. ^{1}H NMR (500Mz, CDCl$_3$): δ 7.71(s, broad, 1H, -CH=CH-), 7.57(s, broad, 2H, aromatic), 7.38(s, broad, 3H, aromatic), 6.51(s, broad, 1H, -CH=CH-), 4.12-4.37(m, 4H, OCH$_2$CH$_2$O), 2.06(s, sharp, 3H, OCH$_3$), 1.85-0.92 (m, 5H, CCH$_3$, -CH$_2$-).

Example 6: Preparation of random copolymer poly(cinnamoylethyl methacrylate-*co*-acetoxyethylmethacrylate) [P(CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)]

[0106] Poly(hydroxyethyl methacrylate) (2.0 g, M_w = 20,000 g/mol, hydroxyl group: 15.4 mmol) was dissolved in 20 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (1.46 g, 8.76 mmol) in 4 mL of anhydrous THF. The reaction was stirred at room temperature for 30 minutes, after which 3 mL of acetic anhydride (excess) were added to cap the free OH groups on the polymer. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold MeOH. The polymer precipitates were purified by repetitive precipitation to give about 2 g of a random copolymer poly(cinnamoylethyl methacrylate-*co*-acetoxyethylmethacrylate) [P(CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)] as a white solid.

[0107] ^{1}H NMR verified the copolymer ratio as 57%:43%. ^{1}H NMR (500Mz, CDCl$_3$): δ 7.67(d, broad, 1H, -CH=CH-), 7.54(s, broad, 2H, aromatic), 7.36(s, broad, 3H, aromatic), 6.48(s, broad, 1H, -CH=CH-), 4.16-4.32(d, 4H, OCH$_2$CH$_2$O), 2.04(s, sharp, 3H, OCH$_3$), 1.85-0.92 (m, 5H, CCH$_3$, -CH$_2$-).

Example 7: Preparation of random copolymer poly(cinnamoylethyl methacrylate-*co*-acetoxyethylmethacrylate) [P(CyEMA$_{0.80}$-*co*-AcEMA$_{0.20}$)]

[0108] Poly(hydroxyethyl methacrylate) (3.0 g, M_w = 20,000 g/mol, hydroxyl group: 23mmol) was dissolved in 30 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (3.07 g, 18.4 mmol) in 4 mL of anhydrous THF. The reaction was stirred at room temperature for 6 hours, after which 3 mL of acetic anhydride (excess) were added to cap the free OH groups on the polymer. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold MeOH. The polymer precipitates were purified by repetitive precipitation to give about 3 g of a random copolymer poly(cinnamoylethyl methacrylate-*co*-acetoxyethylmethacrylate) [P($CyEMA_{0.80}$-*co*-$AcEMA_{0.20}$)] as a white solid.

[0109] ^{1}H NMR verified the copolymer ratio as 80%:20%. ^{1}H NMR (500Mz, $CDCl_3$): δ 7.68(d, broad, 1H, -CH=CH-), 7.53(s, broad, 2H, aromatic), 7.35(s, broad, 3H, aromatic), 6.47(s, broad, 1H, -CH=CH-), 4.14-4.30(m, 4H, OCH_2CH_2O), 2.02(s, sharp, 3H, OCH_3), 1.83-0.93 (m, 5H, CCH_3, $-CH_2-$).

Example 8: Preparation of random copolymer poly(cinnamoylethyl methacrylate-*co*-(trifluoroacetoxy)ethyl methacrylate) [P($CyEMA_{0.57}$-*co*-$TFAcEMA_{0.43}$)]

[0110] Poly(hydroxyethyl methacrylate) (2.0 g, M_w = 20,000 g/mol, hydroxyl group: 15.4mmol) was dissolved in 20 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (1.46 g, 8.76 mmol) in 4 mL of anhydrous THF. The reaction was stirred at room temperature for 3 hours, after which 3 mL of trifluoroacetic anhydride (excess) were added to cap the free OH groups on the polymer. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold MeOH. The polymer precipitates were purified by repetitive precipitation to give about 2 g of a random copolymer poly(cinnamoylethyl methacrylate-*co*-(trifluoroacetoxy)ethyl methacrylate) [P($CyEMA_{0.57}$-*co*-$TFAcEMA_{0.43}$)] as a white solid.

[0111] ^{1}H NMR verified the copolymer ratio as 57%:43%. ^{1}H NMR (500Mz, $CDCl_3$): δ 7.69(d, 1H, -CH=CH-), 7.54(s, broad, 2H, aromatic), 7.36(s, broad, 3H, aromatic), 6.47(broad, 1H, -CH=CH-), 3.73-4.33(m, 4H, OCH_2CH_2O), 1.93-0.94 (m, 5H, CCH_3, $-CH_2-$).

Example 9: Preparation of random copolymer poly(cinnamoylethyl methacrylate-*co*-(pentafluorobenzoyl)ethylmethacrylate) [P(CyEMA$_{0.57}$-*co*-F5BEMA$_{0.43}$)]

[0112] Poly(hydroxyethyl methacrylate) (2 g, M_w = 20,000 g/mol, hydroxyl group: 15.4 mmol) was dissolved in 20 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of cinnamoyl chloride (1.46 g, 8.76 mmol) in 4 mL of anhydrous THF. The reaction was stirred at room temperature for 3 hours, after which 3 mL of pentafluorobenzoyl chloride (excess) were added to cap the free OH groups on the polymer. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold MeOH. The polymer precipitates were purified by repetitive precipitation to give about 2 g of a random copolymer poly(cinnamoylethyl methacrylate-*co*-(pentafluorobenzoyl)ethylmethacrylate) [P(CyEMA$_{0.57}$-*co*-F5BEMA$_{0.43}$)] as a white solid.

[0113] ^{1}H NMR verified the copolymer ratio as 57%:43%. ^{1}H NMR (500Mz, $CDCl_3$): δ 7.64(d, 1H, -CH=CH-), 7.52(s, broad, 2H, aromatic), 7.35(s, broad, 3H, aromatic), 6.44(broad, 1H, -CH=CH-), 4.15-4.47(m, 4H, OCH_2CH_2O), 0.88-1.83(m, 5H, CCH_3, $-CH_2-$).

Example 10: Preparation of random copolymer poly(3-(trifluoromethyl)-cinnamoylethylmethacrylate-*co*-acetoxyethyl methacrylate) [P(CF3CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)]

[0114] Poly(hydroxyethyl methacrylate) (2 g, M_w = 20,000 g/mol, hydroxyl group: 15.4 mmol) was dissolved in 20 mL of anhydrous pyridine. The solution was placed in an ice bath for 10 minutes, followed by addition of a solution of 3-trifluoromethyl cinnamoyl chloride (2.06 g, 8.76 mmol) in 4 mL of anhydrous THF. The reaction was stirred at room temperature for 3 hours, after which 3 mL of acetic anhydride (excess) were added to cap the free OH groups on the polymer. The reaction was stirred at room temperature overnight, then precipitated in about 200 mL of cold MeOH. The polymer precipitates were purified by repetitive precipitation to give about 2 g of a random copolymer poly(3-(trifluoromethyl)-cinnamoylethylmethacrylate-*co*-acetoxyethyl methacrylate) [P(CF3CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)] as a white solid.

[0115] ^{1}H NMR verified the copolymer ratio 57%:43%. ^{1}H NMR (500Mz, $CDCl_3$): ^{1}H NMR (500Mz, $CDCl_3$): δ 7.81-7.29(m, broad, 4H, aromatic, -CH=CH-), 6.56(broad, 1H, -CH=CH-), 4.18-4.35(m, 4H, OCH_2CH_2O), 2.04(s, 3H, OCH_3) 1.92-0.90 (m, 5H, CCH_3, $-CH_2-$).

Example 11: Preparation of capped poly(cinnamoylethylmethacrylate) [CAP-P(CyEMA)]

[0116] **P(CyEMA)** (3.0 g, Example 2) was dissolved in 30 mL of freshly distilled THF and the resulting solution was cooled into an ice-water bath. Trifluoroacetic anhydride (0.5 g) was added dropwise under vigorous stirring in the absence of light. The reaction was warmed to ambient temperature, stirred for 3 hours, and concentrated to dryness under reduced pressure. The resulted solid was dissolved in 30 mL freshly distilled THF and the resulting solution cooled in an ice-water bath. A second portion of trifluoroacetic anhydride (0.5 g) was added dropwise under vigorous stirring. The reaction was warmed to ambient temperature, stirred overnight, and concentrated under reduced pressure. The residue was dissolved in THF and precipitated by addition of methanol, dissolved again in THF and precipitated by addition of diethylether, and the resulting solid was dried under vacuum to provide **CAP- P(CyEMA)** as a white foam (yield >95%).

Example 12: Surface morphology of spin-coated dielectric films

[0117] The photopolymers from Examples 1-3 were dissolved in dioxane to give a solution having a concentration of 80 mg/mL, respectively. The polymer solutions were then spin-coated onto clean silicon substrates between 1300 rpm (acceleration 20). After the spin-coating step, the resulting dielectric films were treated in a 150W ultraviolet oven for 10 minutes, and then annealed in a vacuum oven at 100°C for 10 minutes to completely remove any residual solvent. Film thickness and surface smoothness (represented by root mean square (RMS) roughness) were determined by profilometry and atomic force microscopy (AFM), respectively. The results showed that the polymer films of the present teachings are very smooth, with RMS roughness being in the range of about 0.4 nm.

Example 13: Dielectric properties of spin-coated dielectric films

[0118] Metal-insulator-semiconductor (MIS) capacitor structures were fabricated using the resulting dielectric films from Example 11, and capacitance of the dielectric films was measured. For MIS structure fabrication, heavily doped n-type Si (MEMC Electronic Materials, Antimony/n-doped) was used as the semiconductor onto which the dielectric film was spin-coated to form the insulating layer. Top Au electrodes (area 1 = 100 μm x100 μm; area 2 = 200 μm x 200 μm; area 3 = 500 μm x 1000 μm; area 4 = 1000 μm x 1000 μm; area 5 = 1 cm x 2 cm) were then vacuum deposited on top of the photopolymer insulator at < $1x10^{-6}$ Torr to complete the MIS capacitor structure. Using a shadow mask, rectangular- or square-shaped Au pads having a feature size ranging from 100 μm x 100 μm to 1000 μm x 1000 μm, can be deposited to form MIS structures of different sizes. Unless otherwise specified, leakage currents in this and following examples were determined using capacitor structures with Au pads having a feature size of 200 μm x 200 μm. The J-E characteristics of capacitors based on the dielectric materials of the present teachings appear to be independent of the area of the Au pads, as shown in **Figure 1**.

[0119] The current (I)-voltage (V) responses of the MIS structures were measured using a high sensitivity Keithley 6430 Sub-Femtoamp Source Meter with Remote Preampifier, operated by a local Labview program and general purpose interface bus communication. All of the measurements were performed in ambient atmosphere (relative humidity = 30-80%). To minimize electrical noise during the I-V scan, a triaxial cabling and probing system (Signatone, Gilroy, CA) was employed to probe the MIS structures. The combined use of the Signatone triaxial probing system and the Keithley 6430 source meter reduced the noise level to as low as 10^{-15} A and provided accurate current measurements as low as 10^{-14} A. During the measurement, the bottom electrode was probed with an instrument ground and the top Au pads were probed with a soft tip from the Triaxial probe connected to the Keithley source meter. As controlled by the Labview program, an I-V scan was performed by applying bias to the traixial probe and measuring current through the circuit. The scan rate was between 5-15 s/step, which was controlled by setting the delay time to between 0.5 s and 2 s and the number of measurements per step between 10 and 20.

[0120] The leakage current density (J) (I / area of Au pads) versus electric field (E) (V / thickness of dielectric layer) plots are shown in **Figure 2**. The J-E responses of dielectric films prepared from PVP, PMMA, and PCyVP are included for comparison.

[0121] Similar MIS capacitor structures and test procedures were used to characterize photopolymers from Examples 4 to 10. The leakage current density (J) versus electric field (E) plots are shown in **Figure 3**, along with comparison data from polymers of Examples 2 and 3. The dielectric properties, i.e., leakage current density, capacitance (C_i), and breakdown voltage (BV), as well as film thickness of the aforementioned examples are summarized in **Table 1.**

Table 1. Dielectric properties of different photopolymer-based dielectric films.

Photopolymer	Leakage current density (A/cm^2) at 2 MV/cm	Leakage current density (A/cm^2) at 4 MV/cm	C$_i$ (nF/cm^2)	Thickness (nm)	BV (V)
P(CyVP$_{0.55}$-*co*-MMA$_{0.45}$)	2x10^{-9}	1x10^{-8}	6.4	470	>200
CAP- P(CyVP$_{0.55}$-*co*-MMA$_{0.45}$)	1x10^{-9}	4x10^{-9}	6.3	470	>200
P(CP$_{0.3}$-*co*-CyVP$_{0.25}$-*co*-MMA$_{0.45}$)	3x10^{-8}	3x10^{-6}	6.8	440	>200
P(CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)	2x10^{-9}	6x10^{-8}	7.1	410	>200
P(CyEMA$_{0.8}$-*co*-AcEMA$_{0.2}$)	2x10^{-9}	4x10^{-8}	7.3	400	>200
P(CyEMA)	2x10^{-9}	1x10^{-8}	6.0	460	>200
CAP- P(CyEMA)	1x10^{-9}	4x10^{-9}	6.0	460	>200
P(CyEMA$_{0.57}$-*co*-F5BEMA$_{0.43}$)	2x10^{-9}	1x10^{-8}	6.0	440	>200
P(CF3CyEMA$_{0.57}$-*co*-AcEMA$_{0.43}$)	7x10^{-9}	2x10^{-7}	6.9	430	>200
P(CyEMA$_{0.57}$-*co*-TFAcEMA$_{0.43}$)	6x10^{-9}	3x10^{-7}	6.9	480	>200
P(CyEMA$_{0.5}$-*co*-AcEMA$_{0.5}$) (High MW)	4x10^{-9}	4x10^{-8}	7.8	400	>200
PVP	6x10^{-7}	Break down	6.5	570	150V
PMMA	7x10^{-9}	1x10^{-7}	12	250	>200
PCyVP	2x10^{-8}	1x10^{-6}	9.5	300	>200
Crosslinkable polymer dielectrics reported in the literature	>1x10^{-7}	N/A	N/A	N/A	N/A

Example 14: Device performance of pentacene-based OFETs fabricated with spin-coated dielectric films

[0122] Pentacene OFETs were fabricated with dielectric films from Examples 11 and 12 on both silicon and aluminium gate materials. Specifically, the silicon substrates were highly n-doped silicon wafers obtained from Montco Silicon Tech, Inc. (Spring City, PA) and cleaned by sonication in organic solvents before use. The aluminium substrates were cut from Al-coated plastic substrates. Pentacene was purchased from Sigma-Aldrich (St. Louis, MO) and vacuum-deposited at about 2 x 10^{-6} Torr (500 Å, 0.3 Å/s) while maintaining the substrate temperature at about 50°C to about 70°C. Gold (Au) electrodes were vacuum-deposited through shadow masks at 3-4 x 10^{-6} Torr (500 Å, 0.3 Å/s). The channel length was 50 μm, and the channel width was 5000 μm. These OFETs were found to perform very well, with mobility (μ) approximating 0.5 cm^2/Vs, an $I_{on}:I_{off}$ ratio up to $2x10^7$, negligible hysteresis, and extremely low gate leakage currents. Representative OFET transfer and output plots are shown in **Figure 4** (P($CyEMA_{0.57}$-co-$F5BEMA_{0.43}$) is used as the dielectric layer). OFET performances of these photopolymer-based devices are summarized in **Table 2**. A comparative pentacene OFET device was fabricated using silicon oxide (SiO_2) as the dielectric material. The silicon oxide film has a thickness of 300 nm. The carrier mobilities of this comparative device were found to be about 0.1 cm^2/Vs to about 0.3 cm^2/Vs.

Table 2. Pentacene field-effect transistor parameters for TFT devices based on polymeric dielectric materials of the present teachings. (*Carrier mobility was calculated in saturation.)

Polymer #	Substrate	μ (cm^2/Vs)	$I_{on}:I_{off}$	Gate leakage (nA)
P($CyVP_{0.55}$-*co*-$MMA_{0.45}$)	Si	0.3	$2x10^6$	10
P($CP_{0.3}$-*co*-$CyVP_{0.25}$-*co*-$MMA_{0.45}$)	Si	0.3	$2x10^6$	100
P($CyEMA_{0.57}$-*co*-$AcEMA_{0.43}$)	Si	0.8	$1x10^6$	100
P($CyEMA_{0.8}$-*co*-$AcEMA_{0.2}$)	Si	0.7	$3x10^6$	40
P(CyEMA)	Si	1.0	$2x10^7$	3
CAP-P(CyEMA)	Si	1.2	$4x10^7$	2
P($CyEMA_{0.57}$-*co*-$F5BEMA_{0.43}$)	Si	1.2	$1x10^7$	1000
P($CF3CyEMA_{0.57}$-*co*-$AcEMA_{0.43}$)	Si	0.3	$5x10^5$	10
P($CyEMA_{0.57}$-*co*-$TFAcEMA_{0.43}$)	Si	0.6	$2x10^6$	20
P($CyEMA_{0.8}$-*co*-$AcEMA_{0.2}$)	Al	0.32	$1x10^6$	1
PCyVP	Si	0.65	$1x10^5$	10000
SiO_2	Si	0.2	$1x10^6$	10

Example 15: Device performance of n-type OFETs fabricated with spin-coated dielectric films

[0123] A perylene-type n-type semiconductor, N,N'-bis(n-octyl)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI-$8CN_2$) was used to fabricate n-type OFET devices with photopolymers of the present teachings as the dielectric layer. Specifically, the silicon substrates were highly n-doped silicon wafers obtained from Montco Silicon Tech, Inc. (Spring City, PA) and cleaned by sonication in organic solvents before use. PDI-8CN_2 was synthesized according to procedures described in U.S. Patent Application Publication No. 2005/0176970, and vacuum-deposited at about 2 x 10^{-6} Torr (500 Å, 0.3 Å/s) while maintaining the substrate temperature at about 100°C to about 110°C. Au electrodes were vacuum-deposited through shadow masks at 3-4 x 10^{-6} Torr (500 Å, 0.3 Å/s). The channel length was 50 μm, and the channel width was 5000 μm. These OFETs were found to perform very well, with n-type mobility (μ) approximating 0.05 cm^2/Vs, an I_{on}:I_{off} ratio up to $1x10^4$, negligible hysteresis, and minimal gate leakage currents. Representative OFET transfer and output plots are shown in **Figure 5** (P($CyVP_{0.55}$-*co*-$MMA_{0.45}$) is used as the dielectric layer).

Example 16: Solubility of photopolymer materials before and after photocrosslinking

[0124] Many photopolymers of the present teachings are soluble in common organic solvents including, but not limited to, tetrahydrofuran, bis(2-methoxyethyl) ether, dioxane, chloroform, ethyl acetate, acetone, toluene, dichlorobenzene, cyclohexylbenzene, dimethylformamide, n-methyl pyrrolidone, and cyclohexanone. Photopolymers from Examples 1-10, for example, have excellent solubility in common organic solvents. For instance, P(CyEMA) from Example 2 can be dissolved in ethyl acetate without heating to give a solution having a concentration of 350 mg/mL. Such a solution is sufficiently viscous for use in gravure printing.

[0125] After printing or other solution-phase depositing steps, photopolymers of the present teachings can be cured by exposure to ultraviolet light (e.g., via treatment in a 150 W UV oven for 10 minutes), which renders them insoluble in the organic solvents in which they were initially soluble prior to the photocrosslinking step. The cured dielectric films were found to be robust enough to withstand relatively harsh processes. For example, a photocrosslinked dielectric film was sonicated in dichlorobenzene for 5 minutes, after which its thickness and physical appearance was found to be substantially the same as before the sonication step. This feature of the present dielectric materials makes them attractive candidates for solution-processed bottom-gate OFETs, which requires that the dielectric layer be insoluble in the solution-processing solvent (e.g., dichlorobenzene) for the deposition of the semiconductor layer.

Example 17: Multilayer dielectric material fabricated with spin-coated photopolymer materials

[0126] Since photopolymers of the present teachings can become insoluble in common organic solvents after photocrosslinking, multiple layers of dielectric materials can be coated on top of one another without dissolving the earlier deposited layers. Such multilayer dielectric structures can offer many performance advantages including, but not limited to, minimized pinholes and better uniformity over larger areas.

[0127] MIS capacitor structures and test procedures similar to those described in Example 12 were prepared and used to characterize a two-layer dielectric material prepared from P(CyVP$_{0.55}$-*co*-MMA$_{0.45}$) (Example 3). The leakage current density (J) versus electric field (E) plot is shown in **Figure 6**. While the test pixel shown in Figure 9 has a relatively large area of about 2 cm^2 (typical OFET devices and MIS structures have test pixels generally smaller than 0.01 cm^2), the leakage current density of the tested two-layer dielectric films is still extremely low, indicating excellent film uniformity over large areas. The thickness of the two-layer dielectric film was about 1000 nm, which is two times thicker than the single-layer films (500 nm) of Example 11, implicating the insolubility of the photocrosslinked film during the multilayer coating process.

[0128] Pentacene OFETs were fabricated with the two-layer dielectric films described above. These pentacene OFETS exhibited excellent device performance, as evidenced by hole mobility (μ) of about 0.22 cm^2/Vs, I_{on}:I_{off} ratio of about 3x10^7, negligible hysteresis, and gate leakage current as low as 3 nA at 180 V gate bias. The transfer and output plots are shown in **Figure 7**.

Example 18: Printability of dielectric compositions containing photopolymers

[0129] Using the photopolymer P(CyEMA$_{0.80}$-*co*-AcEMA$_{0.20}$) of Example 7, printable dielectric layers were fabricated. The photopolymer was dissolved in ethyl acetate to give a solution having a concentration of 300 mg/mL solution. Dielectric films were printed using the printing press (IGT), using the gravure mode and the following parameters: Anilox force 100 N, printing speed 0.4 m/s, anilox cylinder 402.100 (40l/cm, copper engraved-chromium plated, stylus 130°, screen angle 53, volume 23.3 mL/m^2). A first layer of the photopolymer was printed on Al-PEN substrate, UV cured for 10 minutes and dried in a vacuum oven for 10 minutes. A second layer of the photopolymer was printed onto the first layer and cured in the same way. MIS capacitor structures and pentacene OFETs were subsequently fabricated. The output and transfer plots of the pentacene OFETs are shown in **Figure 8**.

Example 19: UV curing of the photopolymers

[0130] Selected photopolymers of the present teachings were crosslinked by exposure to ultraviolet light at 254 nm. IR spectroscopy was used to confirm the photocrosslinking of these polymers. The double bond in the cinnamoyl group exhibited characteristic IR absorption at 1630 cm^{-1} before photocrosslinking, and disappeared after the 2+2 cycloaddition photocrosslinking reaction as predicted. **Figure 9** shows the IR absorption spectrum for a photopolymer film before and after UV curing. It could be seen that the intensity of the C=O stretching is significantly reduced after the UV treatment.

Example 20: Low glass transition temperature of the present photopolymers

[0131] The glass transition properties of the present photopolymers were characterized by differential scanning calorimetry (DSC). **Figure 10** shows a typical DSC plot of photopolymers of the present teachings. Additional data for some of the photopolymers are summarized in **Table 3**. For example, the glass transition temperature (T_g) of P(CyEMA$_{0.57}$-*co*-AEMA$_{0.43}$) was measured to be about 45°C (compared to conventional polymeric dielectric material such as PMMA, which has T_g between 80-100°C). Such low glass transition temperature allows a time period for achieving surface planarization and filling of pinholes before initiating the photocrosslinking step to obtain the final photocured crossinked dielectric matrix, which can explain the good film forming properties of photopolymers of the present teachings. Polymers with lower glass transition temperatures (e.g. PMMA, which has T_g between about 80-100°C) typically have better film forming properties compared to polymers with higher glass transition temperatures (e.g., PVP, which has a T_g over 150°C).

Table 3. Glass transition temperatures.

Polymer	**Tg (°C)**
Poly(vinyl phenol), PVP	150
Poly(methylmethacrylate), PMMA	80-100
Poly(vinylphenylcinnamate), PCyVP (Example 1)	100
P(CyEMA) (Example 2)	53
$P(CyEMA_{0.57}$-*co*-$AcEMA_{0.43})$ (Example 6)	45
$P(CyEMA_{0.57}$-co-$F5BEMA_{0.43})$ (Example 9)	56
CAP-P(CyEMA) (Example 11)	53

Example 21: Shelf stability of photopolymer dielectric films

[0132] **Figure 11** shows the leakage current density versus electric field (J-E) plot of an MIS capacitor structure incorporating a dielectric film prepared from $(P(CyVP_{0.55}$-*co*-$MMA_{0.45})$ that had been stored in air for 55 days. It can be seen that, despite the storage period, the photopolymer dielectric film still exhibited excellent dielectric properties, as evidenced by the very low the leakage current density (which actually decreased slightly after 55 days). These results therefore show that the present photopolymer materials possess excellent shelf stability as a dielectric material. As it is recognized, OH group-containing dielectric polymers are typically moisture-sensitive and have limited shelf stability. Without wishing to be bound to any particular theory, it is believed that by derivatizing the photopolymers to decrease the number of OH groups present, photopolymers of the present teachings have improved shelf stability compared to other known polymer dielectric materials such as PVP. Residual OH groups can be capped or masked, for example, by using suitable reagents, including trifluoroacetic anhydride (*e.g.*, Example 11) or trifluoroacetyl chloride.

Example 22: Exclusively solution-processed OFET

[0133] Completely solution-processed OFETs were fabricated using photopolymers of the present teachings as the dielectric layer and a drop-casted n-type perylene material as the semiconductor layer. It is believed that this was the first n-type OFET device fabricated that had both the semiconductor layer and the dielectric layer deposited from solution.

[0134] A perylene-based n-type semiconductor, N,N'-bis(n-octyl)-dicyanoperylene-3,4:9,10-bis(dicarboximide) (PDI-8CN_2), was dropcasted from a dichlorobenzene solution (2 mg/mL) on a solution-deposited and then crosslinked photopolymer dielectric layer (700 nm) on a Si substrate. The substrate was maintained at 105°C, during which the solvent was evaporated to yield a crystalline semiconductor film. OFET devices were fabricated and tested using procedures similar to those described in the previous examples. Representative transfer and output plots are shown in **Figure 12**. The exclusively solution-processed OFETs exhibited good device performance: N-type mobility was calculated to be as high as 0.035 cm^2/Vs, $I_{on}:I_{off}$ ratio was measured to be about $1x10^4$, and gate leakage current was measured to be less than or about 50 nA. These results show that the present photopolymer-based dielectric materials have excellent insolubility against the solvents used in the solution processes used to deposit the semiconductor layer, and that the present photopolymer-based dielectric materials have good compatibility with solution-processed n-type semiconductor materials.

Example 23: Photopolymer dielectric thin films

[0135] **Figure 13** shows the J-E plot of a 100 nm thick photopolymer dielectric film. The data presented in Figure 14 show comparable leakage current density compared to the 400 nm to 500 nm photopolymer dielectric films demonstrated in the earlier examples. It can be seen that the breakdown field of such a thin film can be as high as 7 MV/cm.

Example 24: Effect of OH groups in photopolymer structures on leakage current density

[0136] The leakage current density vs electric field plots of P($CyVP_{0.55}$-*co*-$MMA_{0.45}$) (Example 3) and P($VP_{0.30}$-*co*-$CyVP_{0.25}$-*co*-$MMA_{0.45}$) (Example 4) are compared in **Figure 14**. It can be seen that the leakage current density of P($CyVP_{0.55}$-*co*-$MMA_{0.45}$) is about two orders of magnitude lower that of P($VP_{0.30}$-

co-$CyVP_{0.25}$-co-$MMA_{0.45}$). Since a main difference between the two polymers is that P($VP_{0.30}$-co-$CyVP_{0.25}$-co-$MMA_{0.45}$) has significant amount of OH groups while P($CyVP_{0.55}$-co-$MMA_{0.45}$) has almost none, these data suggest that OH groups can have dramatic effect on the leakage current density of dielectric polymers. Additional capping or masking of the residual OH groups (*e.g.*, Example 11) can further reduce leakage current density and stabilize electrical performance under ambient conditions.

Example 25: Effect of photo-patterning on dielectric properties

[0137] A spincoated photopolymer film [P(CyEMA) in Example 2] was exposed to ultraviolet light (254 nm) through a shadow mask and then washed with THF and dried. The film exhibited a clear pattern negative to that of the shadow mask. Au electrodes were then evaporated on top of the exposed and crosslinked region of the film to fabricate an MIS capacitor structure, the leakage current of which was tested using similar procedures as described earlier. **Figure 15** shows the leakage current density vs electric field plot of such a dielectric film. The J-E response of a similar dielectric film without any photo patterning/solvent rinsing treatment also was shown in the figure for comparison. It can be seen that the leakage current of the patterned dielectric film was comparable to the unpatterned dielectric film.

[0138] In another experiment, parallel Au lines were deposited on a Si substrate, after which a photopolymer film [P(CyEMA) in Example 2] was spincoated on top of the Au lines. The photopolymer film was exposed to ultraviolet light (254 nm) through a shadow mask with line-shape openings perpendicular to the underlying Au lines. The photopolymer film was washed with THF and dried. The resulting film has rectangular-shaped "via holes" at the intersections of Au lines and photo mask lines. To test if the "via holes" were free of photopolymer residues, another layer of Au electrode was deposited on top the "via holes" and the interconnect resistance at the "via holes" was estimated to be < 5 ohm.

[0139] These two experiments show that the photopolymer dielectric materials can be easily integrated with circuitry fabrication processes, including photo patterning and "via hole" patterning processes.

Example 26: Bottom-contact bottom-gate OFETs with a photopolymer dielectric layer

[0140] **Figure 16** illustrates the four common types of OFET structures: top-contact bottom-gate structure **(a)**, bottom-contact bottom-gate structure **(b)**, bottom-contact top-gate structure **(c)**, and top-contact top-gate structure **(d)**. As shown in **Figure 16**, an OFET can include a dielectric layer (e.g., shown as 8, 8', 8", and 8'" in **Figure 16a, 16b, 16c,** and **16d**, respectively), a semiconductor layer (e.g., shown as 6, 6', 6", and 6'" in **Figure 16a, 16b, 16c,** and **16d**, respectively), a gate contact (e.g., shown as 10, 10', 10", and 10'" in **Figure 16a, 16b, 16c,** and **16d**, respectively), a substrate (e.g., shown as 12, 12', 12", and 12'" in **Figure 16a, 16b, 16c,** and **16d,** respectively), and source and drain contacts (e.g., shown as 2, 2', 2", 2'", 4, 4', 4", and 4'" in **Figure 16a, 16b, 16c,** and **16d**, respectively). Most of the OFET devices demonstrated in the previous examples have top-contact bottom-gate structures. In this example, bottom-contact bottom-gate OFETs were fabricated using a dielectric material of the present teachings [P(CyEMA) in Example 2] as the insulating layer. First, a dielectric film was fabricated on a Si substrate with a thickness of about 900 nm. Au (25 nm) was evaporated onto the photopolymer film through a shadow mask to form source and drain electrodes, which were then treated in saturated alkylthiol ethanol solution for 1 hour. Pentacene (50 nm) was then evaporated on top (the substrate temperature was 60°C) to complete the bottom-contact device. The transfer and output plots of such a bottom-contact device are shown in **Figure 17**. Hole mobility of about 0.074 cm^2/Vs and an I_{on}/I_{off} ratio of about $1x10^7$ were obtained.

Example 27: Bottom-contact top-gate OFETs with a photopolymer dielectric layer

[0141] In this example, bottom-contact top-gate OFETs were fabricated using a dielectric material of the present teachings [P(CyEMA) from Example 2] as the dielectric layer. First, Au (25 nm) was evaporated onto an insulating substrate (SiO_2) through a shadow mask to form source and drain electrodes, which were then treated in saturated alkylthiol ethanol solution for 1 hour. Second, pentacene (50 nm) was evaporated on top to form the semiconductor layer. Photopolymer films were then spin-coated on top of pentacene as the dielectric layer followed by deposition of Au as the gate electrode. The transfer plot of such a bottom-contact top-gate device is shown in **Figure 18**. Hole mobility of about 0.01 cm^2/Vs and an I_{on}/I_{off} ratio of about $3x10^3$ were obtained.

Example 28: Top-contact OFETs with a photopolymer dielectric layer and a conducting polymer as the bottom-gate electrode

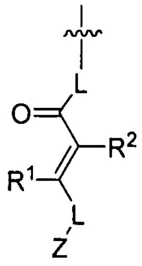
[0142] In this example, top-contact OFETs were fabricated using a dielectric material of the present teachings [P($CyVP_{0.55}$-*co*-$MMA_{0.45}$) from Example 3] as the dielectric layer and a conducting polymer thin film as the bottom-gate electrode. First, a conducting polymer (PEDOT-PSS, 1:1 ratio) was spin-coated on a $3M^{TM}$ overhead transparency to form the gate electrode. Dielectric and semiconductor layers (n-type semiconductor, N,N'-bis(n-octyl)-dicyanonaphthalene-3,4:9,10-bis(dicarboximide), NDI-$8CN_2$) were then deposited using procedures similar to those described in Example 14. Au (25 nm) was evaporated onto the semiconductor layer to complete the top source and drain electrodes. The OFET characteristics (output plot) of such a top-contact bottom-gate device are shown in **Figure 19**. Electron mobility of about 0.03 cm^2/Vs and an I_{on}/I_{off} ratio of about 10 were obtained.

[0143] The present teachings can be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The foregoing embodiments are therefore to be considered in all respects illustrative rather than limiting on the present teachings described herein. The scope of the present teachings is thus indicated by the appended claims rather than by the foregoing description, and all changes that come within the meaning and range of equivalency of the claims are intended to be embraced therein.

Claims

What is claimed is:

1. A polymer comprising a pendant group having the formula:



wherein:

L, at each occurrence, is independently –Y–, –Y–O–Y–, –Q–, –Y–S–Y–, –Y–C(O)–O–Y–, –Q–C(O)–O–Y–, –Y–O–C(O)–Q–, –Y–O–C(O)–Y–, –Q–C(O)–Q–, –Y–C(O)–Y–, –Q–C(O)–Y–, or –Y–C(O)–Q–;

wherein:

Q, at each occurrence, is $-O-[Y-O]_p-Y-O-$;

Y, at each occurrence, is a divalent C_{1-10} alkyl group, a divalent C_{2-10} alkenyl group, a divalent C_{2-10} alkynyl group, a divalent C_{6-10} aryl group, or a covalent bond, wherein each of the C_{1-10} alkyl group, the C_{2-10} alkenyl group, the C_{2-10} alkynyl group, and the C_{6-10} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN; and

p is an integer in the range of 0 to 10;

R^1 and R^2 are independently H, a halogen, or CN; and

Z is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-20} alkyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, a $-O-C_{1-20}$ haloalkyl group, a $-C(O)-C_{1-6}$ alkyl group, a $-C(O)-C_{1-6}$ haloalkyl group, and a $-C(O)-O-C_{1-6}$ alkyl group;

wherein the polymer has a leakage current density less than about $1\mathrm{x}10^{-8}$ A/cm^2 at 2 MV/cm.

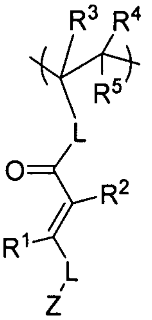
2. The polymer of claim 1, wherein R^1 and R^2 are independently H or F.

3. The polymer of claim 1 or 2, wherein Z is a C_{1-6} alkyl group, a C_{1-6} perfluoroalkyl group, or a phenyl group optionally substituted with 1 to 5 substituents independently selected from F, a C_{1-20} alkyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, and a $-O-C_{1-20}$ haloalkyl group.

4. The polymer of any one of claims 1-3, wherein Z is a phenyl group, a perhalophenyl group, or a phenyl group substituted with a trifluoromethyl group, a C_{1-20} alkoxy group, or a $-O-C_{1-20}$ haloalkyl group.

5. The polymer of any one of claims 1-4, wherein L, at each occurrence, is independently $-O-$, $-C_6H_5-O-$, $-C(O)-O-$, $-C(O)-O-CH_2CH_2-O-$, $-C(O)-O-CF_2CF_2-O-$, or a covalent bond.

6. The polymer of any one of claims 1-5 comprising a repeating unit having the formula:

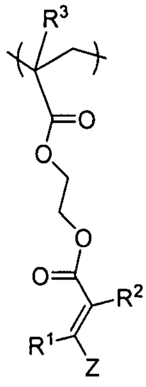


wherein:

R^3, R^4, and R^5 are independently H, a halogen, a C_{1-10} alkyl group, or a C_{6-14} aryl group, wherein each of the C_{1-10} alkyl group and the C_{6-14} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN; and

R^1, R^2, L, and Z are as defined in claim 1.

7. The polymer of claim 6, wherein the repeating unit has a formula selected from: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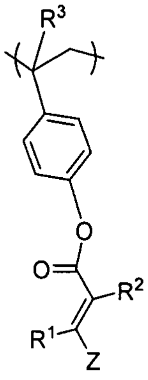
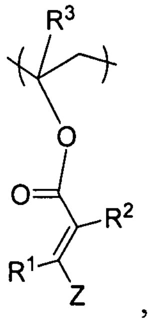

, and

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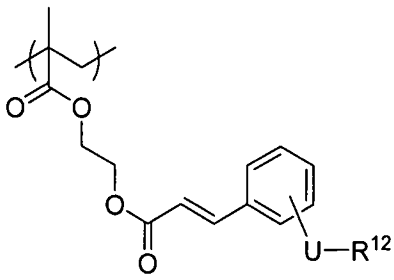
wherein R^1, R^2, R^3, and Z are as defined in claim 1.

8. The polymer of claim 6 or claim 7, wherein the repeating unit has the formula:



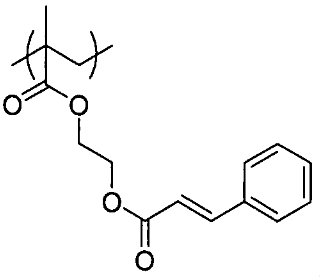
wherein:

U is –Y– or –Y–O–Y–;

R^{12} is H, a C_{1-20} alkyl group, or a C_{1-20} haloalkyl group; and

Y is as defined in claim 1.

9. The polymer of any one of claims 6-8, the repeating unit has a formula selected from: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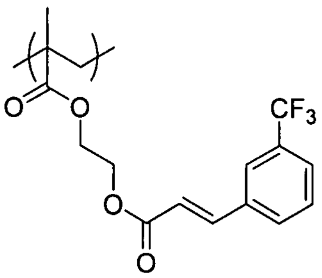
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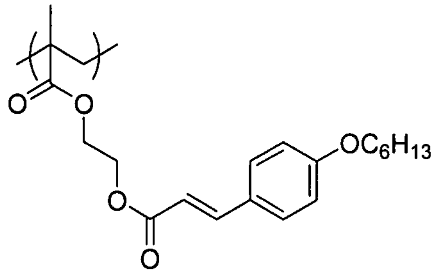

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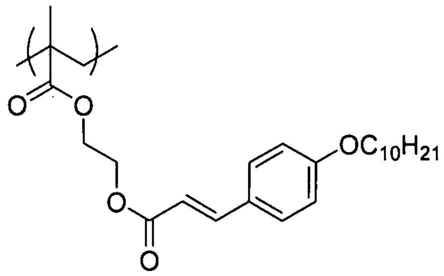

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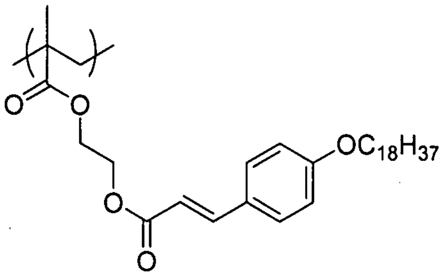

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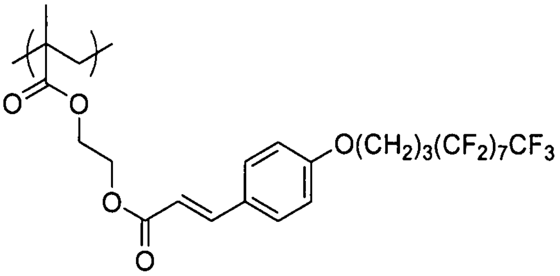

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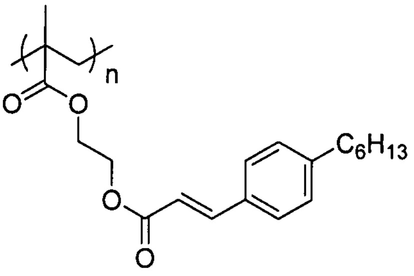

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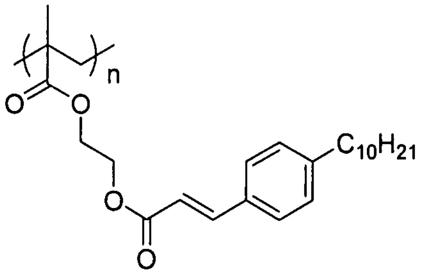

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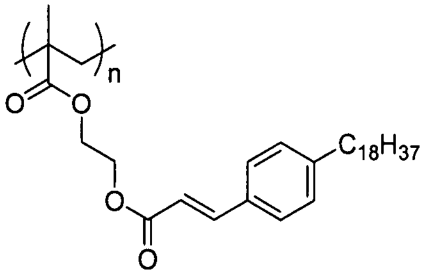
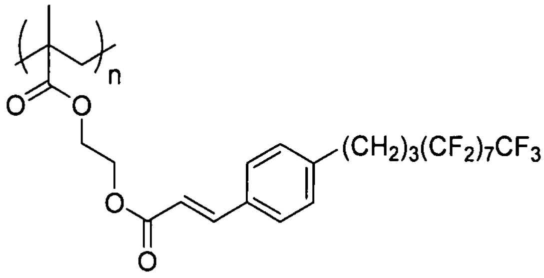


,

and



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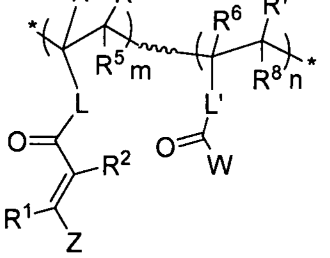
10. The polymer of any one of claims 1-6, the polymer having the formula:



wherein R^6, R^7, and R^8 are independently H, a halogen, a C_{1-10} alkyl group, or a C_{6-14} aryl group, wherein each of the C_{1-10} alkyl group and the C_{6-14} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN;

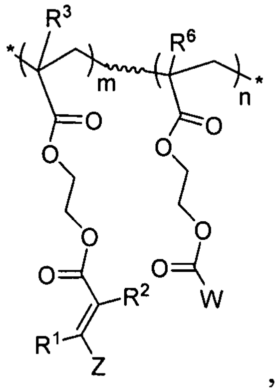
L' is –Y–, –Y–O–Y–, –Q–, –Y–S–Y–, –Y–C(O)–O–Y–, –Q–C(O)–O–Y–, –Y–O–C(O)–Q–, –Y–O–C(O)–Y–, –Q–C(O)–Q–, –Y–C(O)–Y–, –Q–C(O)–Y–, or –Y–C(O)–Q–;

W is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, a C_{1-10} alkoxy group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{1-6} alkoxy group, a –C(O)–C_{1-6} alkyl group, a –C(O)–C_{1-6} haloalkyl group, and a –C(O)–O–C_{1-6} alkyl group;

m and n are independently a real number, wherein $0 < m \leq 1$, $0 \leq n < 1$, and $m + n = 1$; and

R^1, R^2, R^3, R^4, R^5, L, Q, Y, and Z are as defined in claim 1.

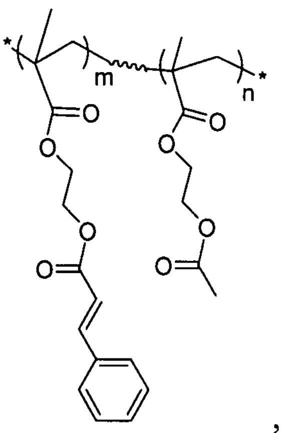
11. The polymer of claim 10, the polymer having the formula:



,

wherein R^1, R^2, R^3, R^6, W, Z, m, and n are as defined in claim 10.

12. The polymer of claim 11, the polymer having a formula selected from: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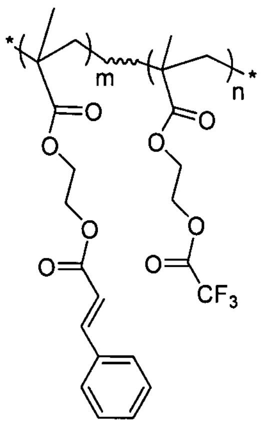
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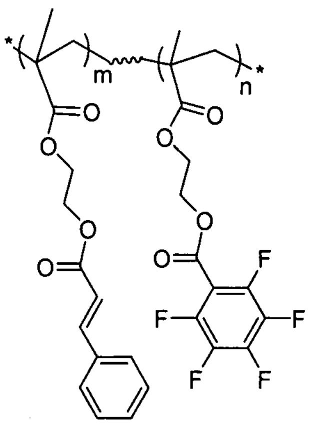
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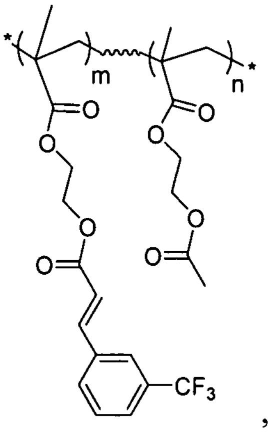
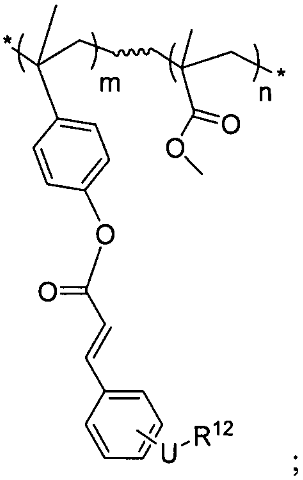

,

wherein m and n are as defined in claim 10.

13. The polymer of claim 10, the polymer having the formula:


;

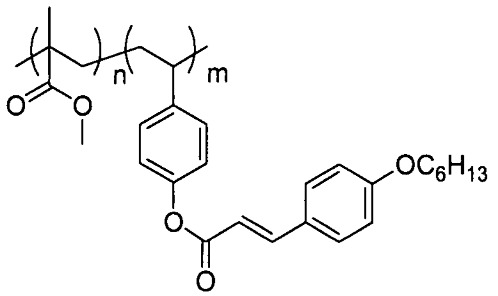
wherein:

U is –Y– or –Y–O–Y–;

R^{12} is H, a C_{1-20} alkyl group, or a C_{1-20} haloalkyl group; and

m, n, and Y are as defined in claim 10.

14. The polymer of claim 13, the polymer having a formula selected from:



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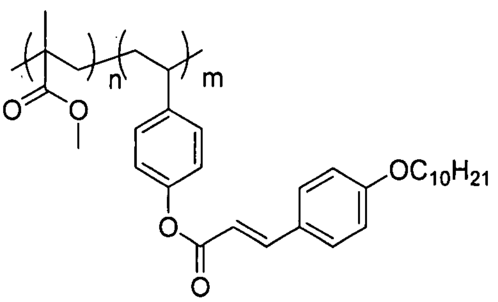

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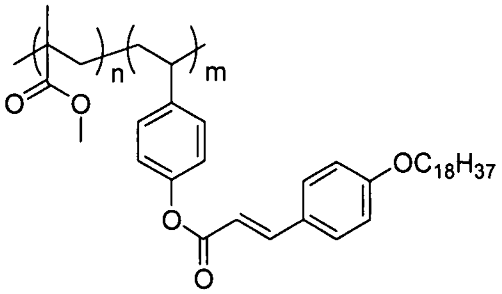

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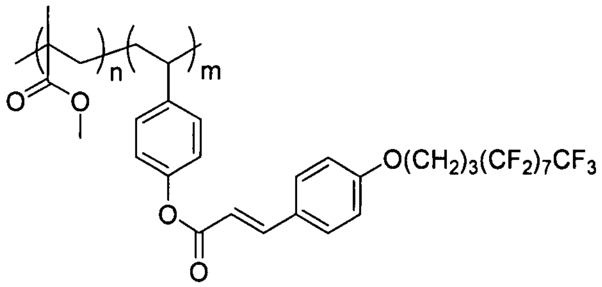

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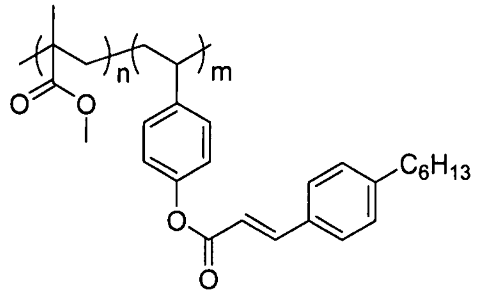

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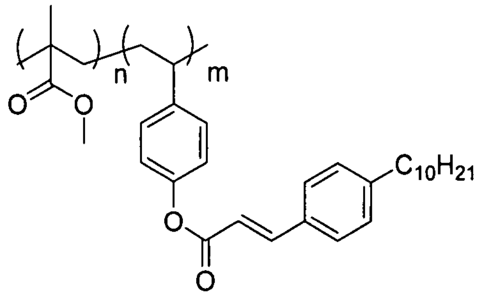

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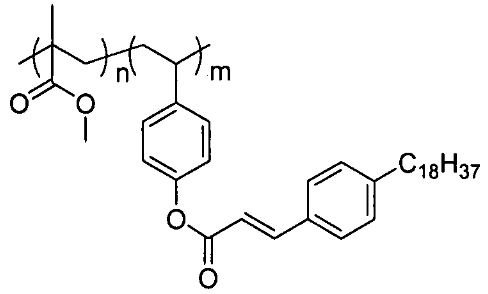

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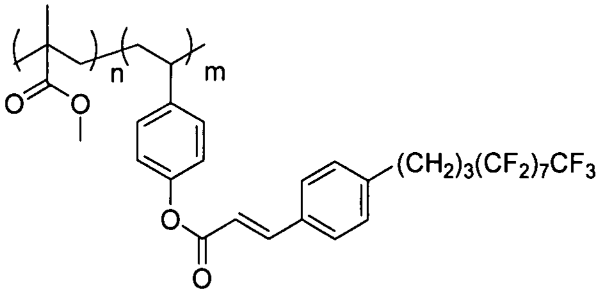
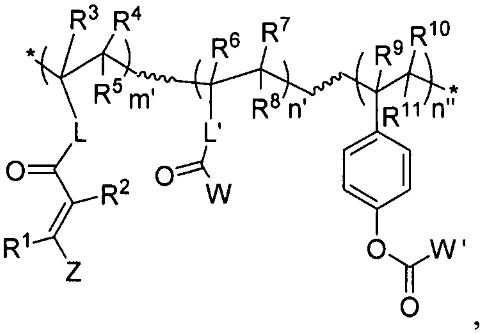
and



;

wherein m and n are as defined in claim 10.

15. The polymer of claim 10, the polymer having the formula:



wherein:

R^9, R^{10}, and R^{11} are independently H, a halogen, a C_{1-10} alkyl group, or a C_{6-14} aryl group, wherein each of the C_{1-10} alkyl group and the C_{6-14} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN;

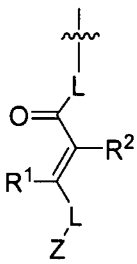
W' is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, a C_{1-10} alkoxy group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-6} alkyl group, a C_{1-6} haloalkyl group, a C_{1-6} alkoxy group, a $-C(O)-C_{1-6}$ alkyl group, a $-C(O)-C_{1-6}$ haloalkyl group, and a $-C(O)-O-C_{1-6}$ alkyl group;

m', n', and n" are independently a real number, wherein $0 < m' \leq 1$, $0 \leq n' < 1$, $0 \leq n'' < 1$, and $m' + n' + n'' = 1$; and

R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, L, L', W, and Z are as defined in claim 10.

16. The polymer of claim 15, wherein W' is CF_3.

17. A polymer comprising a pendant group having the formula:



wherein:

L, at each occurrence, is independently –Y–, –Y–O–Y–, –Q–, –Y–S–Y–, –Y–C(O)–O–Y–, –Q–C(O)–O–Y–, –Y–O–C(O)–Q–, –Y–O–C(O)–Y–, –Q–C(O)–Q–, –Y–C(O)–Y–, –Q–C(O)–Y–, or –Y–C(O)–Q–;

wherein:

Q, at each occurrence, is –O–[Y–O]$_p$–Y–O–;

Y, at each occurrence, is a divalent C_{1-10} alkyl group, a divalent C_{2-10} alkenyl group, a divalent C_{2-10} alkynyl group, a divalent C_{6-10} aryl group, or a covalent bond, wherein each of the C_{1-10} alkyl group, the C_{2-10} alkenyl group, the C_{2-10} alkynyl group, and the C_{6-10} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN; and

p is an integer in the range of 0 to 10;

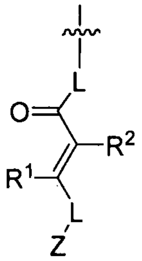
R^1 and R^2 are independently H, a halogen, or CN; and

Z is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-20} alkyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, a –O–C_{1-20} haloalkyl group, a –C(O)–C_{1-6} alkyl group, a –C(O)–C_{1-6} haloalkyl group, and a –C(O)–O–C_{1-6} alkyl group;

wherein the polymer has a glass transition temperature of less than about 100°C.

18. The polymer of claim 17, wherein the polymer has a leakage current density less than about 1×10^{-8} A/cm^2 at 2 MV/cm.

19. A polymer comprising a crosslinked product of a compound having a pendant group of the formula:



wherein:

L, at each occurrence, is independently –Y–, –Y–O–Y–, –Q–, –Y–S–Y–, –Y–C(O)–O–Y–, –Q–C(O)–O–Y–, –Y–O–C(O)–Q–, –Y–O–C(O)–Y–, –Q–C(O)–Q–, –Y–C(O)–Y–, –Q–C(O)–Y–, or –Y–C(O)–Q–;

wherein:

Q, at each occurrence, is –O–[Y–O]$_p$–Y–O–;

Y, at each occurrence, is a divalent C_{1-10} alkyl group, a divalent C_{2-10} alkenyl group, a divalent C_{2-10} alkynyl group, a divalent C_{6-10} aryl group, or a covalent bond, wherein each of the C_{1-10} alkyl group, the C_{2-10} alkenyl group, the C_{2-10} alkynyl group, and the C_{6-10} aryl group is optionally substituted with 1 to 5 substituents independently selected from a halogen and CN; and

p is an integer in the range of 0 to 10;

R^1 and R^2 are independently H, a halogen, or CN; and

Z is a C_{1-10} alkyl group, a C_{1-10} haloalkyl group, or a C_{6-10} aryl group optionally substituted with 1 to 5 substituents independently selected from a halogen, CN, a C_{1-20} alkyl group, a C_{1-20} haloalkyl group, a C_{1-20} alkoxy group, a $-O-C_{1-20}$ haloalkyl group, a $-C(O)-C_{1-6}$ alkyl group, a $-C(O)-C_{1-6}$ haloalkyl group, and a $-C(O)-O-C_{1-6}$ alkyl group.

20. A dielectric composition comprising the polymer of any one of claims 1-18 dissolved in one or more organic solvents.

21. A solution-processable dielectric composition comprising the polymer of any one of claims 1-18 dissolved in one or more organic solvents.

22. A printable dielectric composition comprising the polymer of any one of claims 1-18 dissolved in one or more organic solvents.

23. The dielectric composition of any one of claims 20-22, wherein the one or more organic solvents are selected from tetrahydrofuran, bis(2-methoxyethyl) ether, dioxane, chloroform, ethyl acetate, acetone, toluene, dichlorobenzene, cyclohexylbenzene, dimethylformamide, n-methyl pyrrolidone, and cyclohexanone.

24. A dielectric material comprising the polymer of any one of claims 1-19.

25. A multilayer dielectric material comprising two or more layers of a dielectric material, the dielectric material comprising the polymer of any one of claims 1-19.

26. An electronic device comprising the dielectric material of claim 24 or 25.

27. The electronic device of claim 26, wherein the electronic device is an organic field effect transistor (OFET).

28. The electronic device of claim 26 or 27, wherein the electronic device is a top-contact bottom-gate OFET.

29. The electronic device of claim 26 or 27, wherein the electronic device is a bottom-contact bottom-gate OFET.

30. The electronic device of claim 26 or 27, wherein the electronic device is a bottom-contact top-gate OFET.

31. The electronic device of claim 26 or 27, wherein the electronic device is a top-contact top-gate OFET.

32. The electronic device of any one of claims 26-31, comprising a solution-processable semiconductor layer.

33. The electronic device of any one of claims 26-31, comprising a vapor-deposited semiconductor layer.

34. A method of preparing a dielectric material, the method comprising:

preparing a solution comprising the polymer of any one of claims 1-18;
printing the solution onto a substrate to form a dielectric layer; and
exposing the dielectric layer to radiation to induce crosslinking and create a crosslinked dielectric material.

35. The method of claim 34, comprising:

printing a second dielectric layer onto the crosslinked dielectric layer; and
exposing the second dielectric layer to radiation to induce crosslinking and create a second crosslinked dielectric material to form a multilayer dielectric material.

36. A method of fabricating a top-contact bottom-gate organic field effect transistor, the method comprising:

preparing a solution comprising the polymer of any one of claims 1-18;
printing the solution onto a substrate to form a dielectric layer;
exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material;
forming a semiconductor layer on the crosslinked dielectric material; and

forming a first electrical contact and a second electrical contact on the semiconductor layer.

37. A method of fabricating a bottom-contact bottom-gate organic field effect transistor, the method comprising:

preparing a solution comprising the polymer of any one of claims 1-18;
printing the solution onto a substrate to form a dielectric layer;
exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material;
forming a first electrical contact and a second electrical contact on the crosslinked dielectric material; and
forming a semiconductor layer above the crosslinked dielectric material, the first electrical contact and the second electrical contact.

38. A method of fabricating a bottom-contact top-gate organic field effect transistor, the method comprising:

forming a first electrical contact and a second electrical contact on a substrate;
forming a semiconductor layer above the substrate, the first electrical contact and the second electrical contact;
preparing a solution comprising the polymer of any one of claims 1-18;
printing the solution onto the semiconductor layer to form a dielectric layer;
exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material;
forming a third electrical contact on the crosslinked dielectric material, wherein the third electrical contact is above an area between the first electrical contact and the second electrical contact.

39. A method of fabricating a top-contact top-gate organic field effect transistor, the method comprising:

forming a semiconductor layer on a substrate;
forming a first electrical contact and a second electrical contact on the semiconductor layer;

preparing a solution comprising the polymer of any one of claims 1-18;
printing the solution above the semiconductor layer, the first electrical contact and the second electrical contact, to form a dielectric layer;
exposing the dielectric layer to radiation to induce crosslinking to form a crosslinked dielectric material;
forming a third electrical contact on the crosslinked dielectric material, wherein the third electrical contact is above an area between the first electrical contact and the second electrical contact.

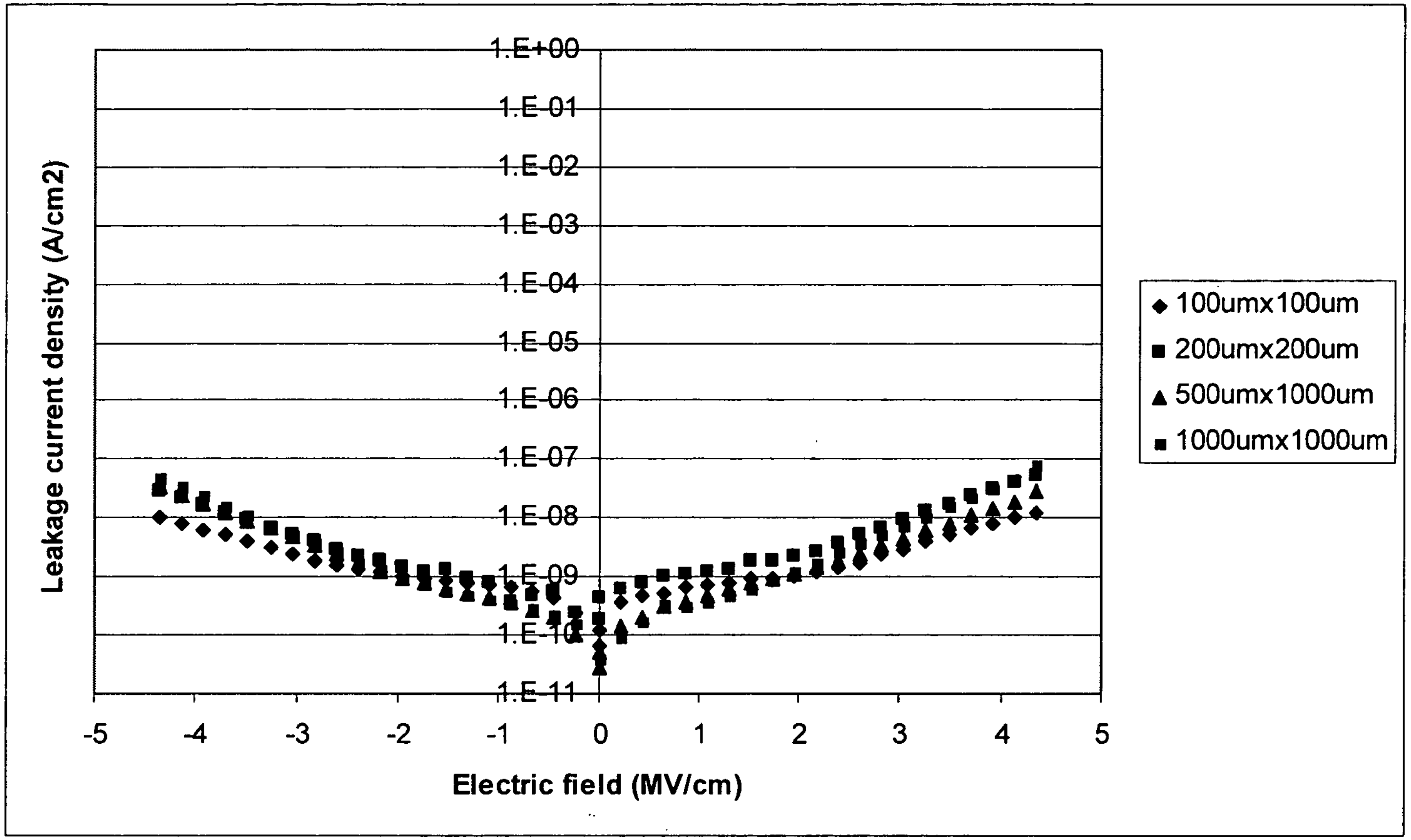

1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
Leakage current density (A/cm2)
-5
-4
-3
-2
-1
0
1
2
3
4
5
Electric field (MV/cm)
◆ 100umx100um
■ 200umx200um
▲ 500umx1000um
■ 1000umx1000um

Figure 1

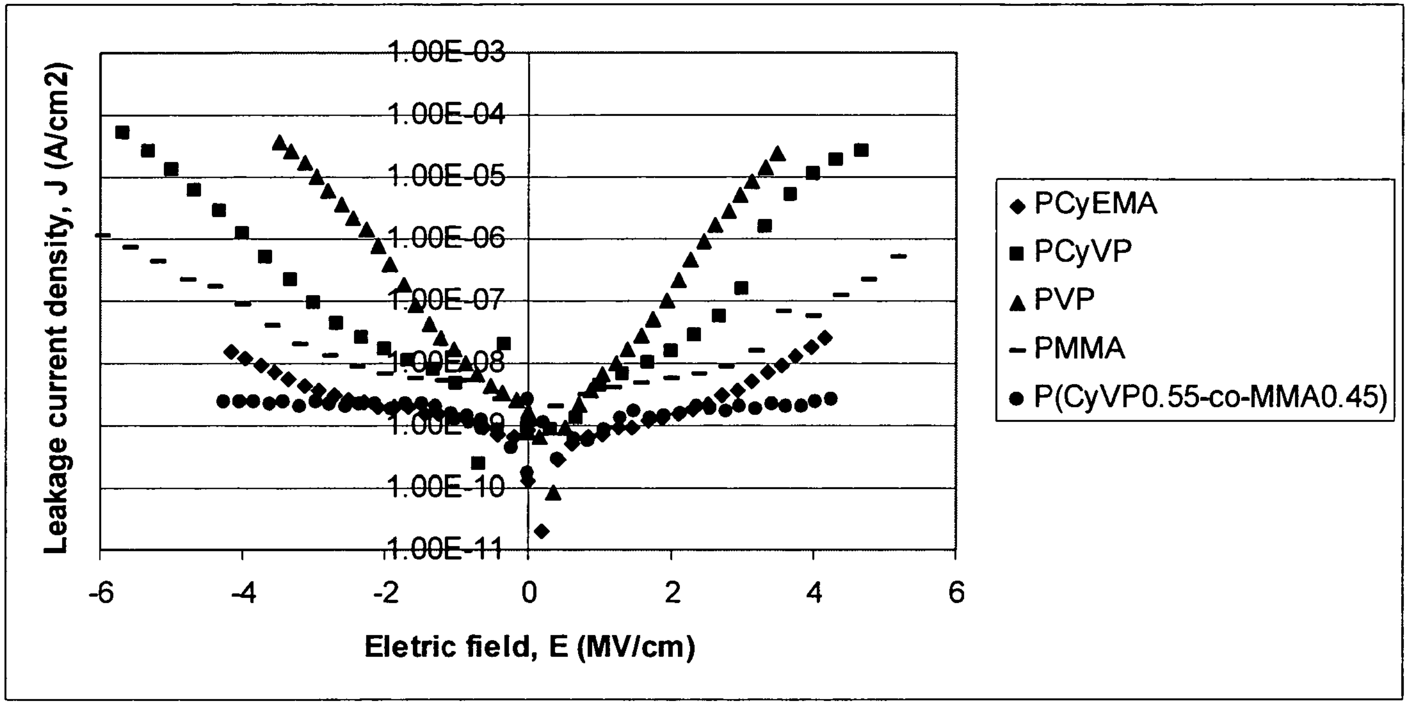

1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
1.00E-09
1.00E-10
1.00E-11
Leakage current density, J (A/cm2)
-6
-4
-2
0
2
4
6
Eletric field, E (MV/cm)
◆ PCyEMA
■ PCyVP
▲ PVP
– PMMA
● P(CyVP0.55-co-MMA0.45)

Figure 2

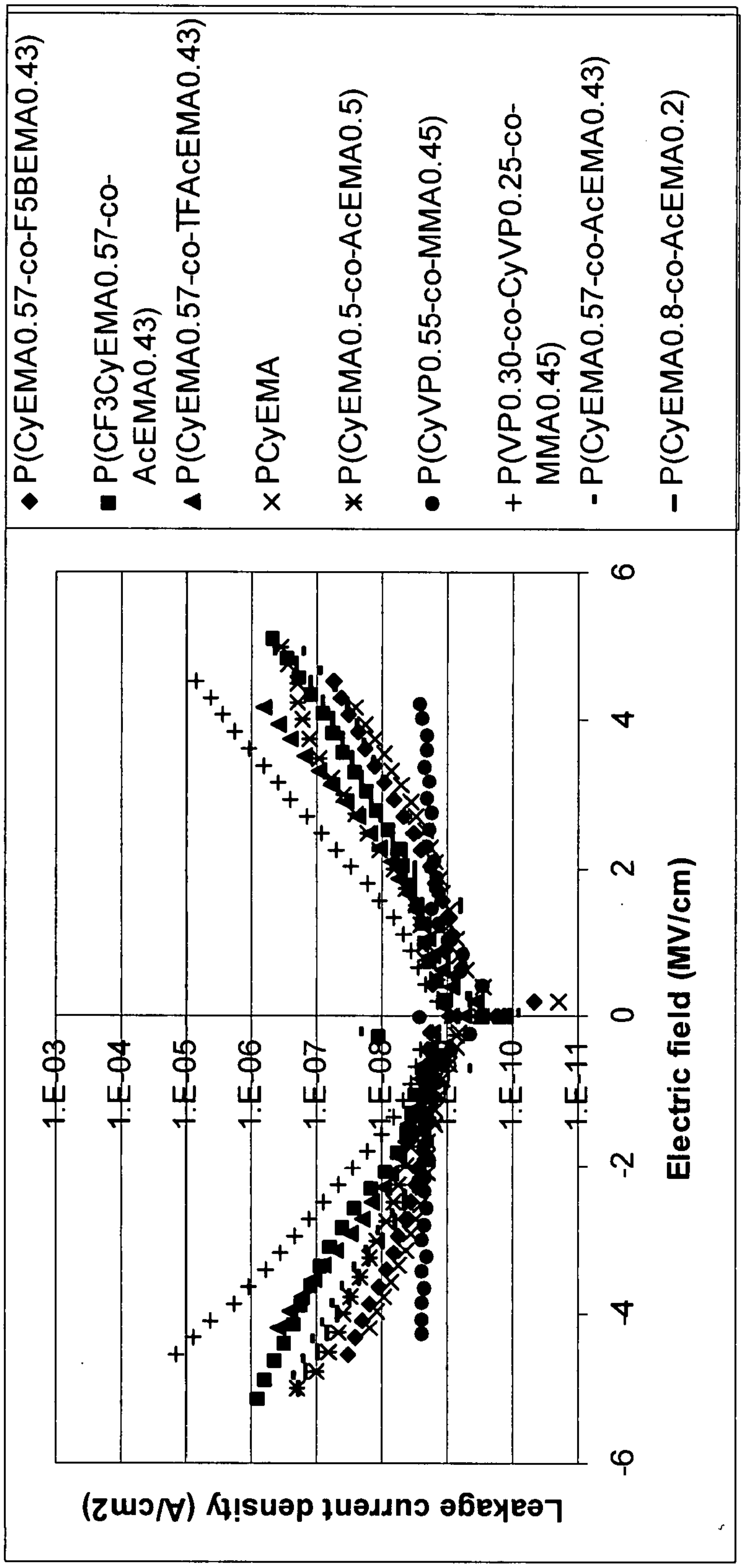
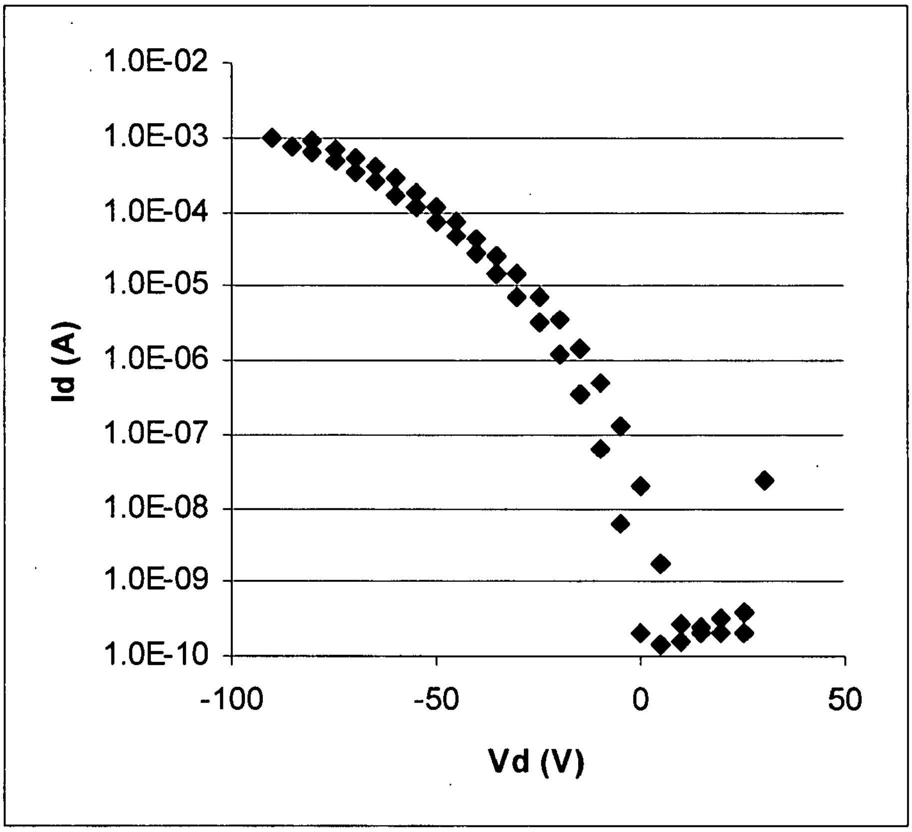
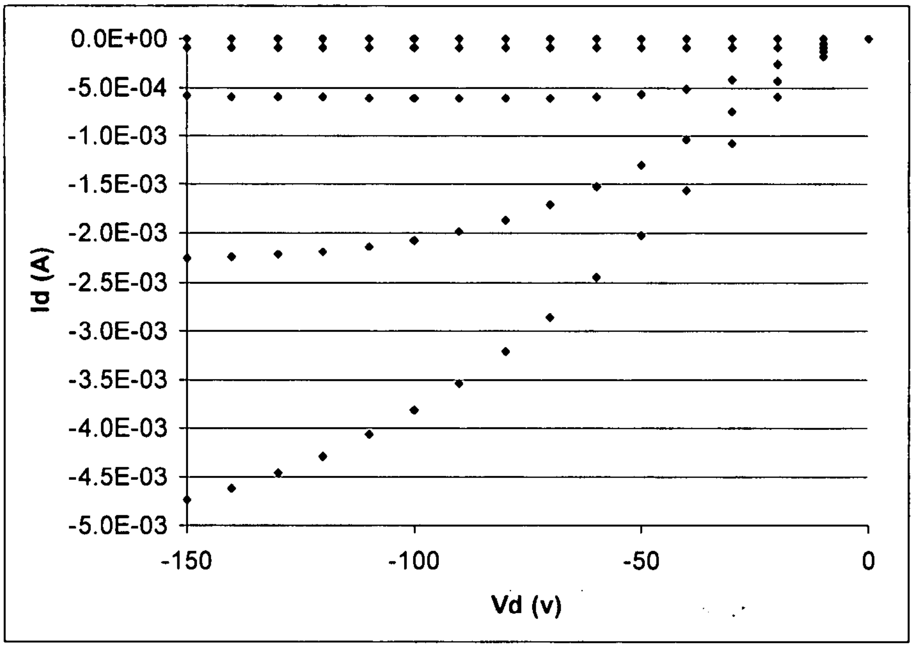

Leakage current density (A/cm2)
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
-6
-4
-2
0
2
4
6
Electric field (MV/cm)
◆ P(CyEMA0.57-co-F5BEMA0.43)
■ P(CF3CyEMA0.57-co-AcEMA0.43)
▲ P(CyEMA0.57-co-TFAcEMA0.43)
× PCyEMA
✻ P(CyEMA0.5-co-AcEMA0.5)
● P(CyVP0.55-co-MMA0.45)
+ P(VP0.30-co-CyVP0.25-co-MMA0.45)
- P(CyEMA0.57-co-AcEMA0.43)
– P(CyEMA0.8-co-AcEMA0.2)

Figure 3

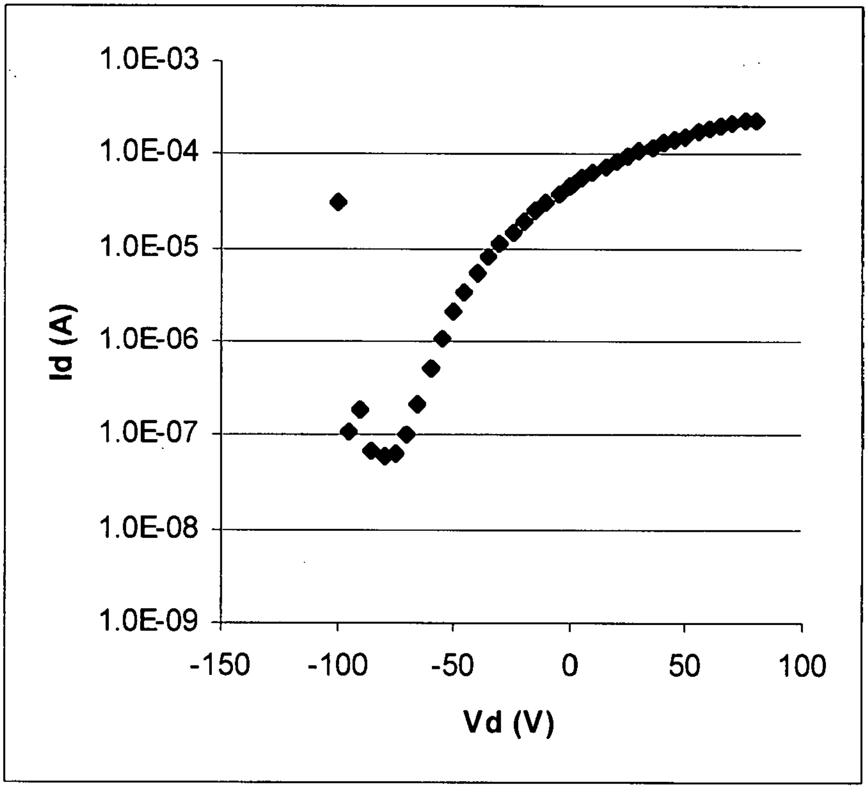


Transfer plot

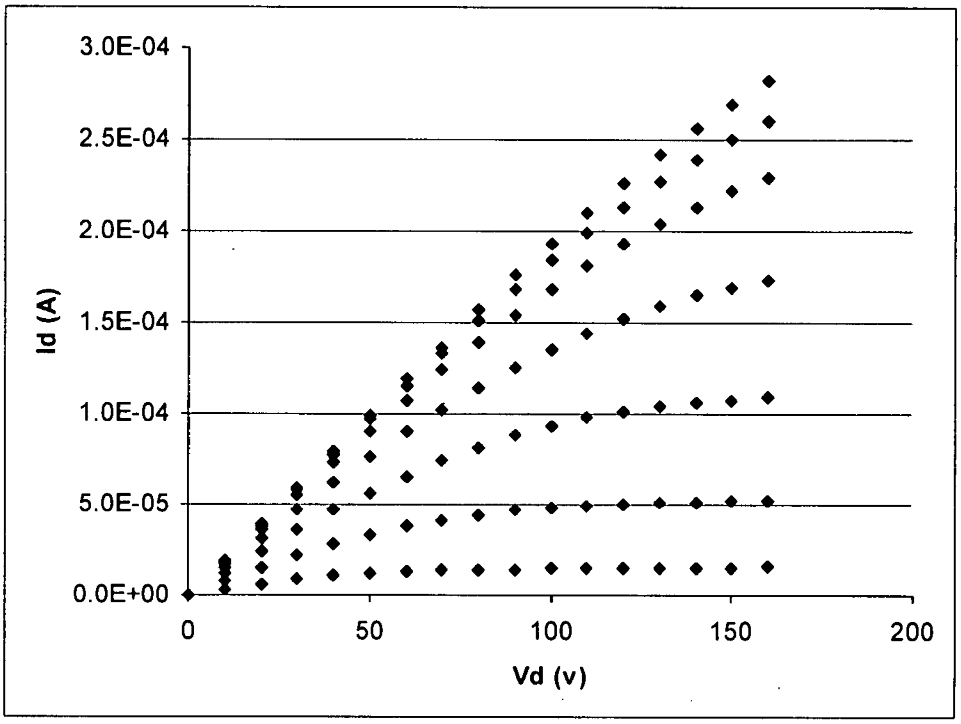


Output plot

Figure 4



Transfer plot



Output plot

Figure 5

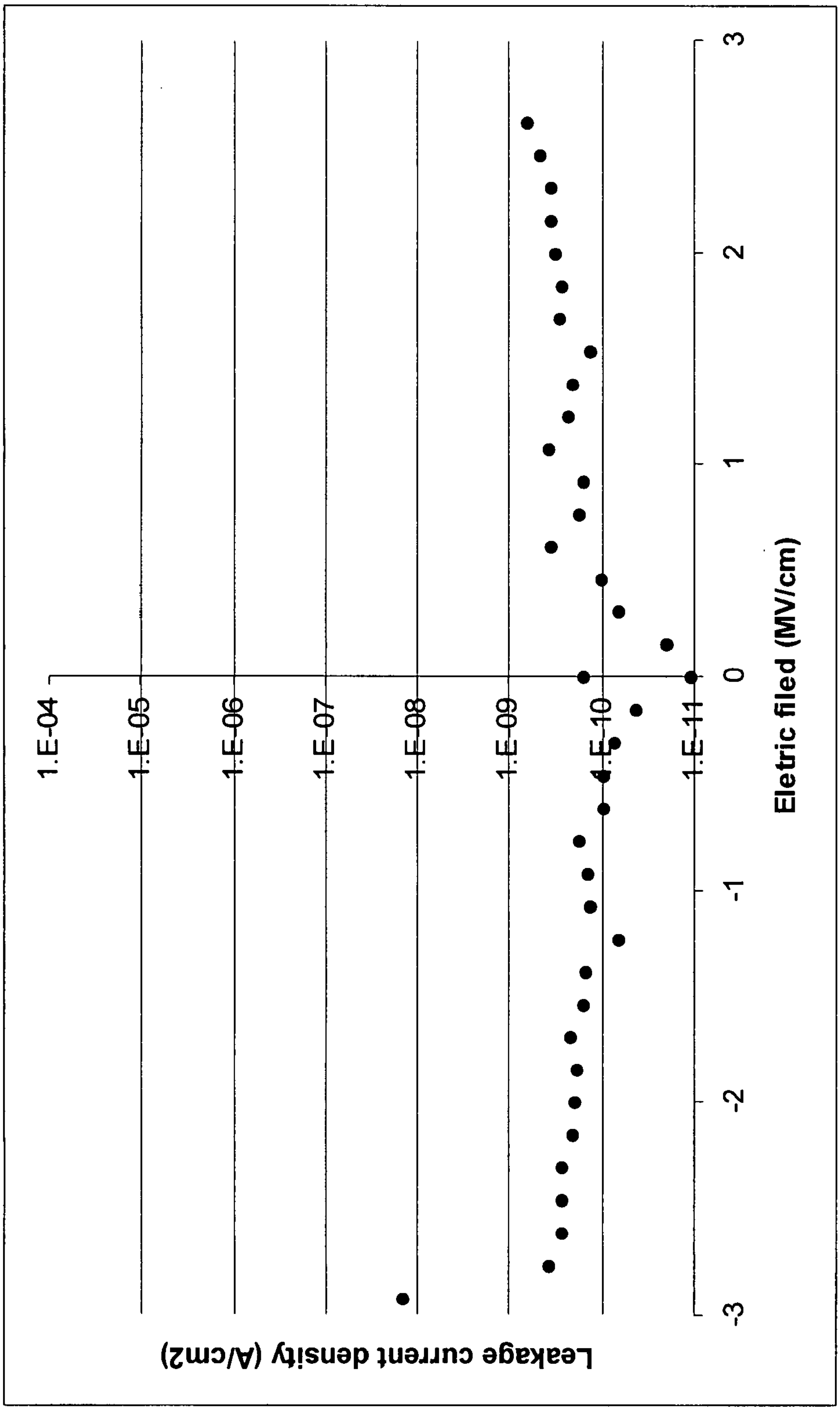
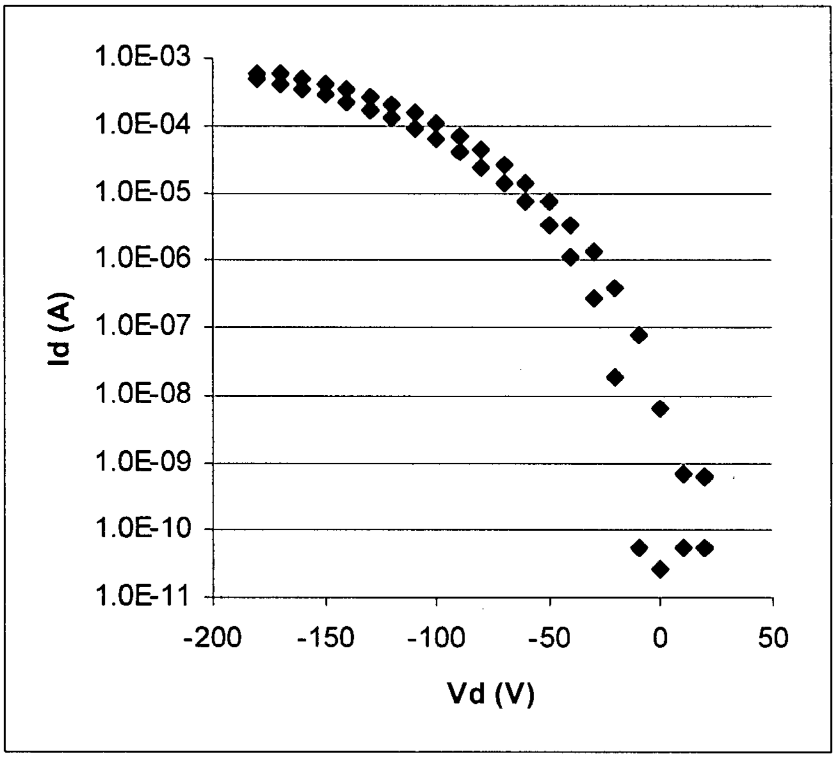
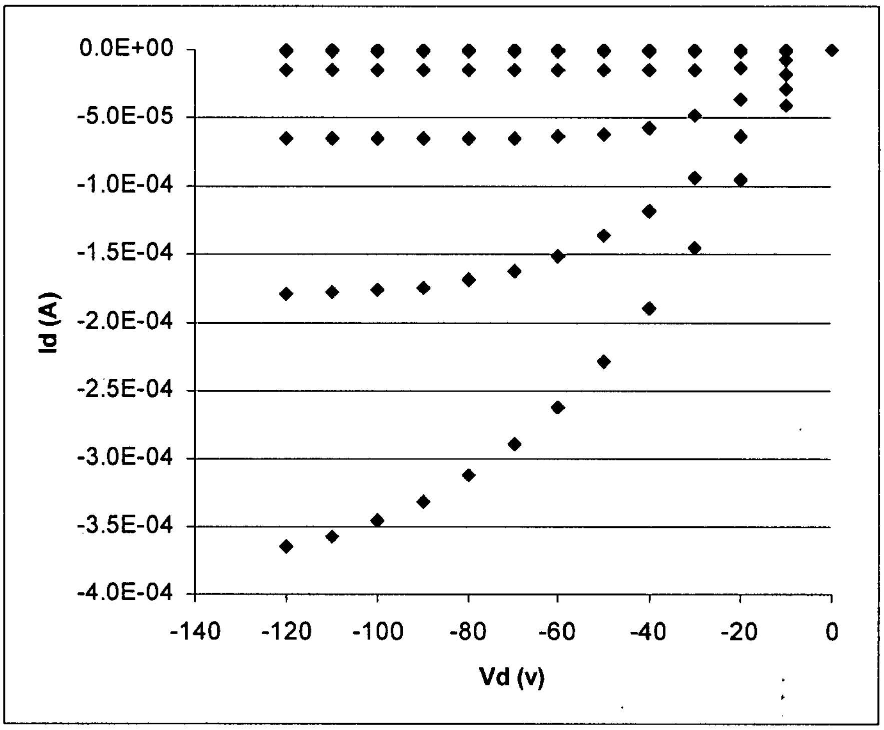

Leakage current density (A/cm2)
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
1.E-11
-3
-2
-1
0
1
2
3
Eletric filed (MV/cm)

Figure 6

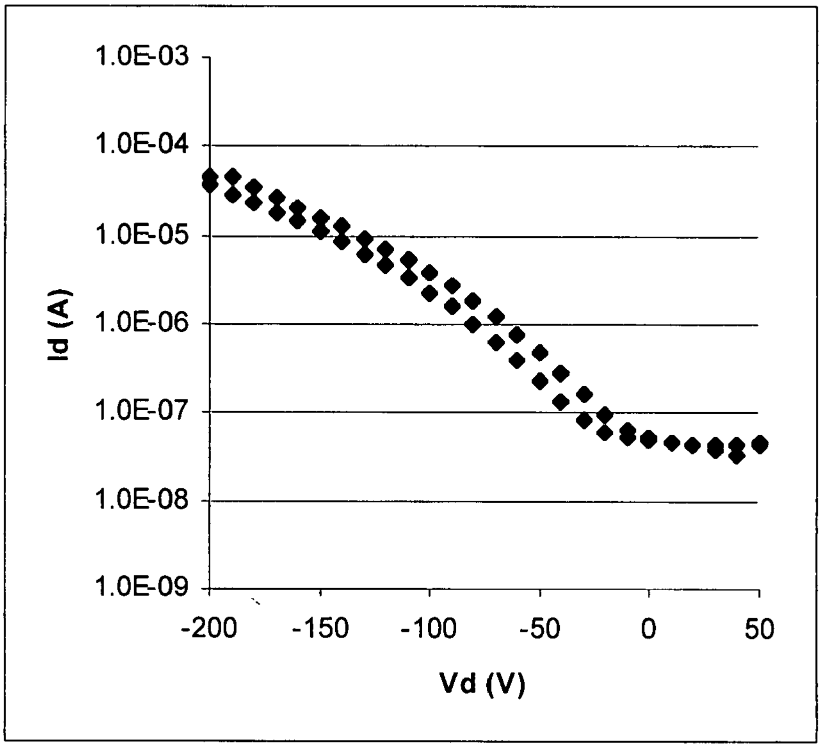


Transfer plot

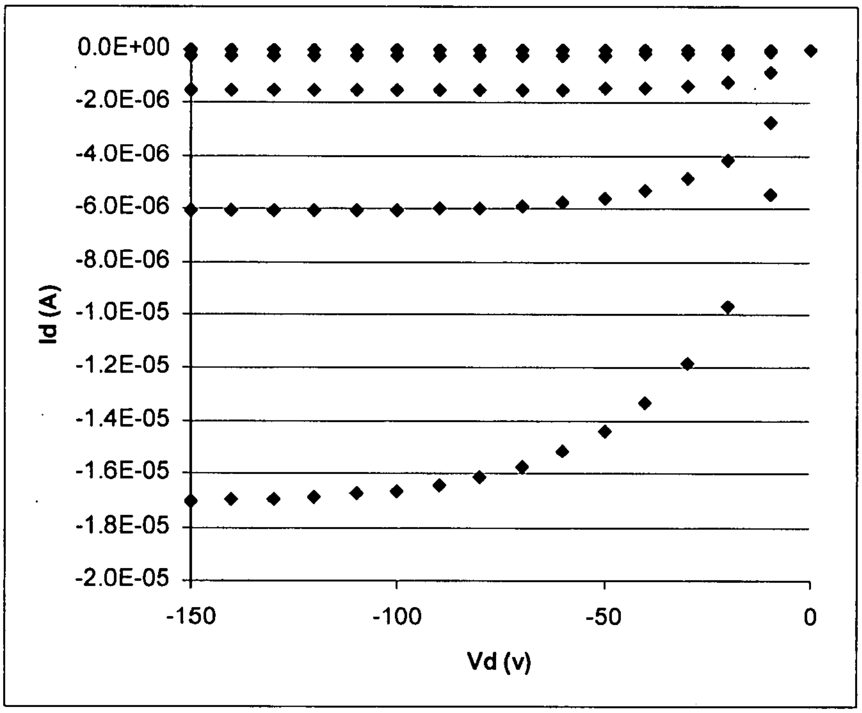


Output plot

Figure 7

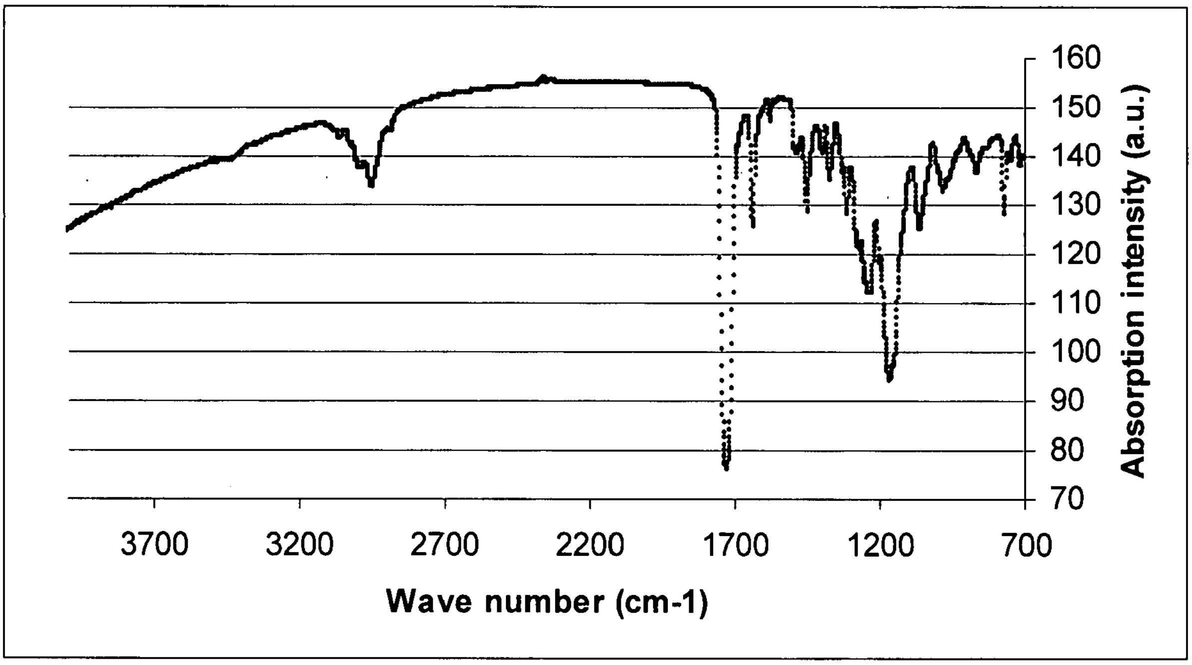


Transfer plot

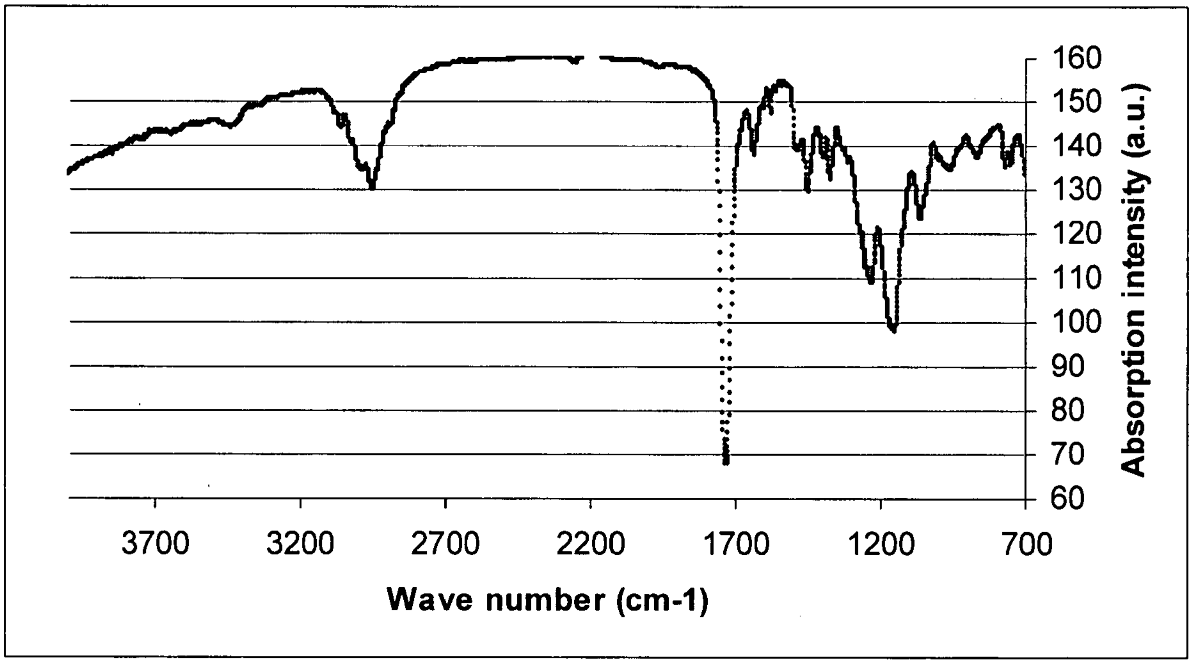


Output plot

Figure 8



Before UV treatment



After UV treatment

Figure 9

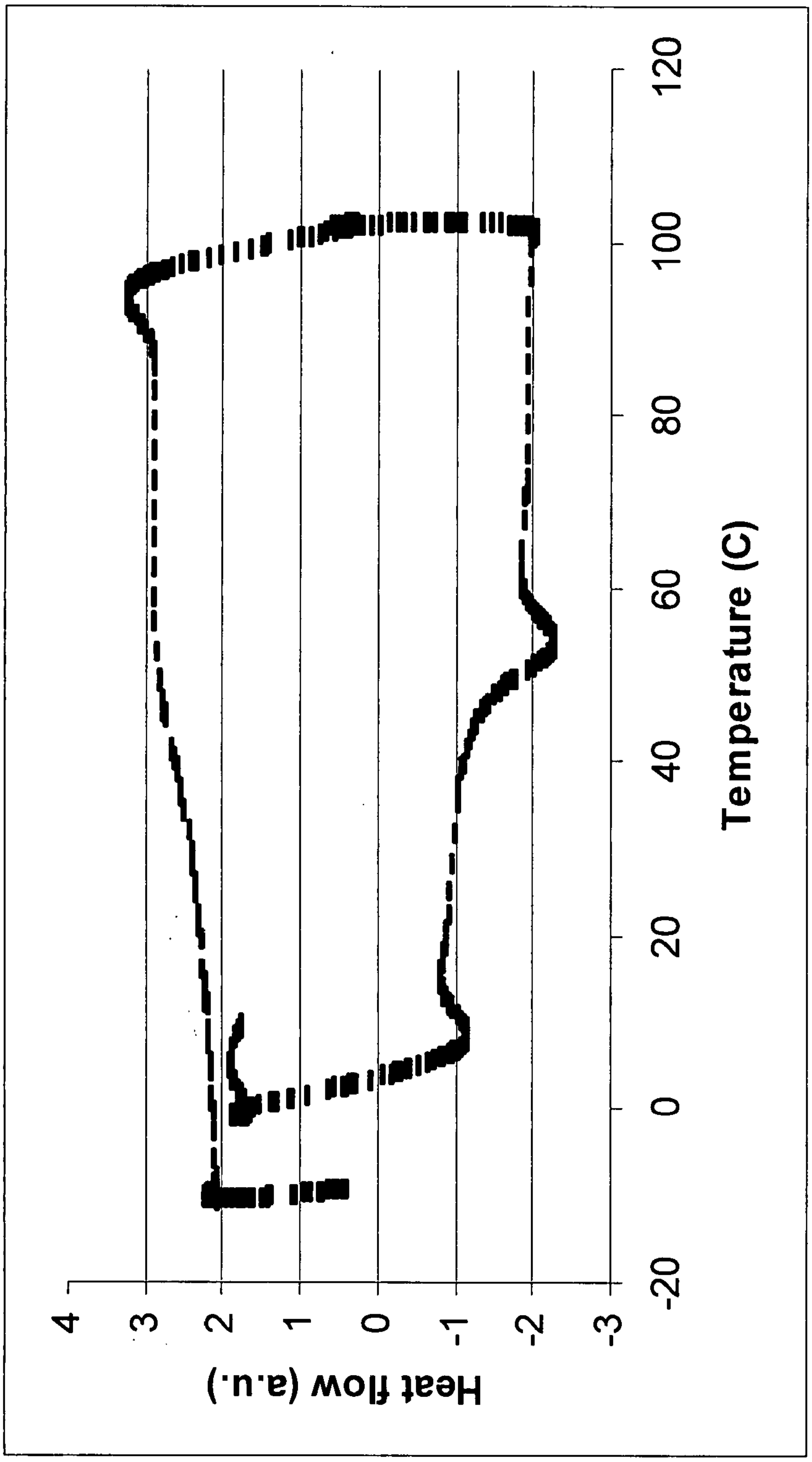


Figure 10

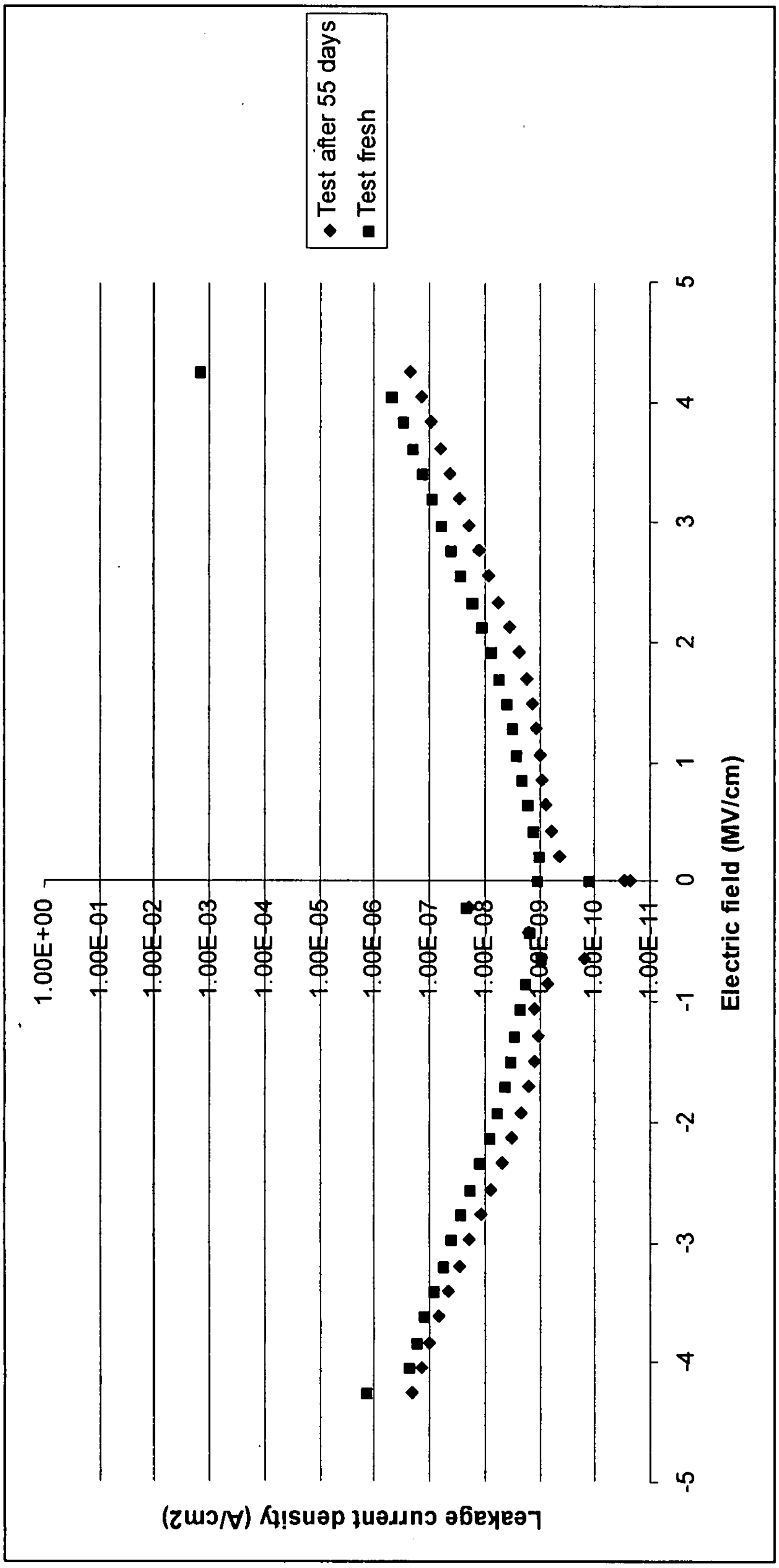
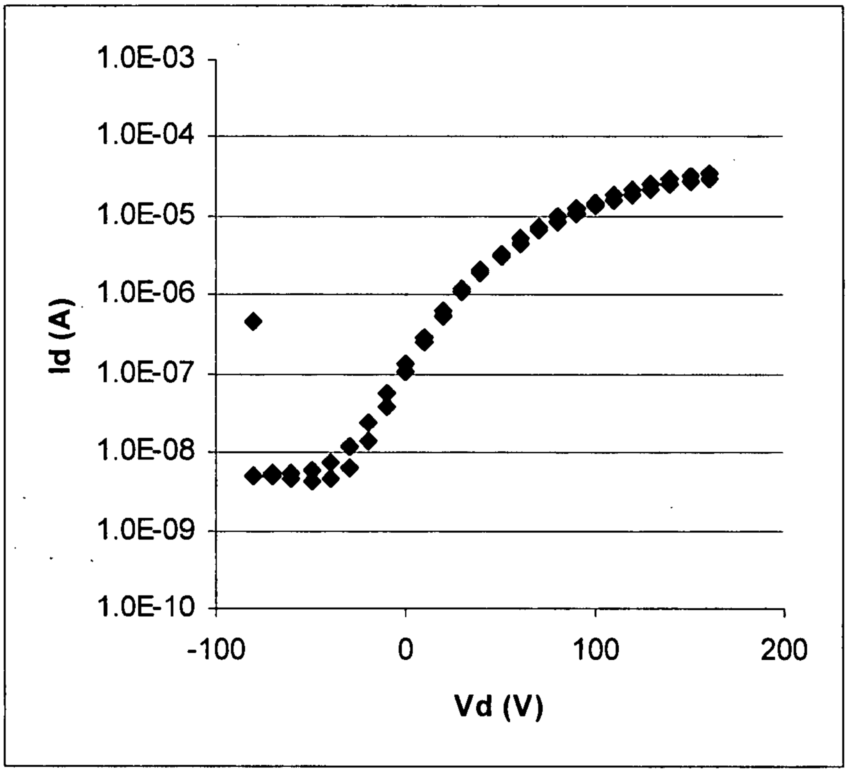
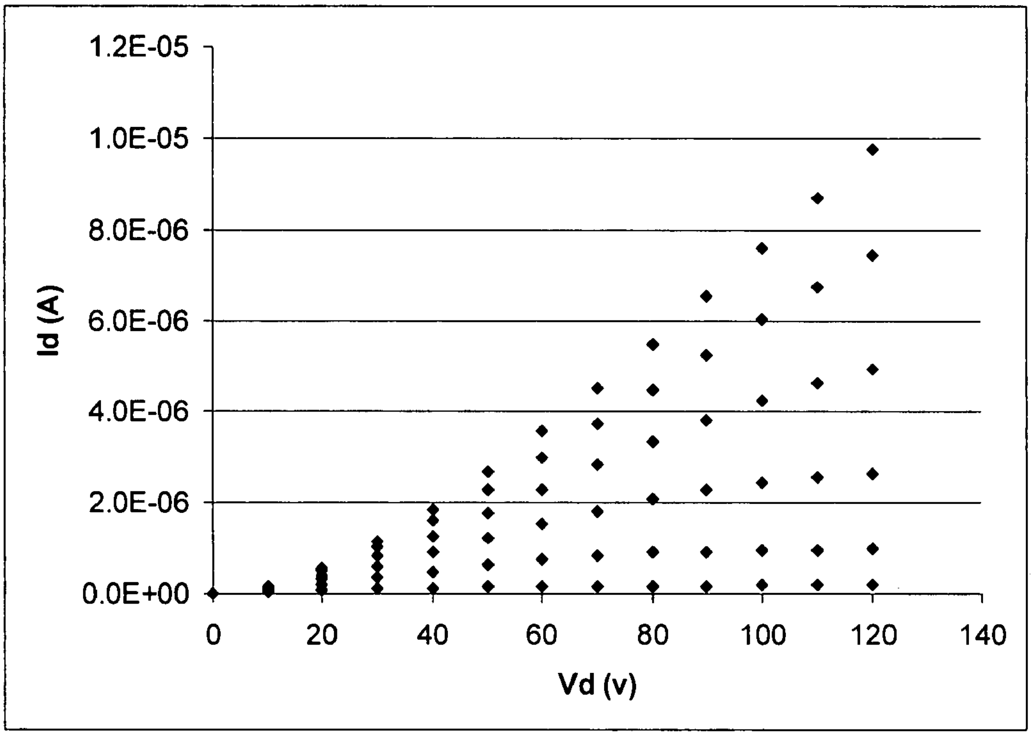

Leakage current density (A/cm2)
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
1.00E-09
1.00E-10
1.00E-11
-5
-4
-3
-2
-1
0
1
2
3
4
5
Electric field (MV/cm)
◆ Test after 55 days
■ Test fresh

Figure 11



Transfer plot



Output plot

Figure 12

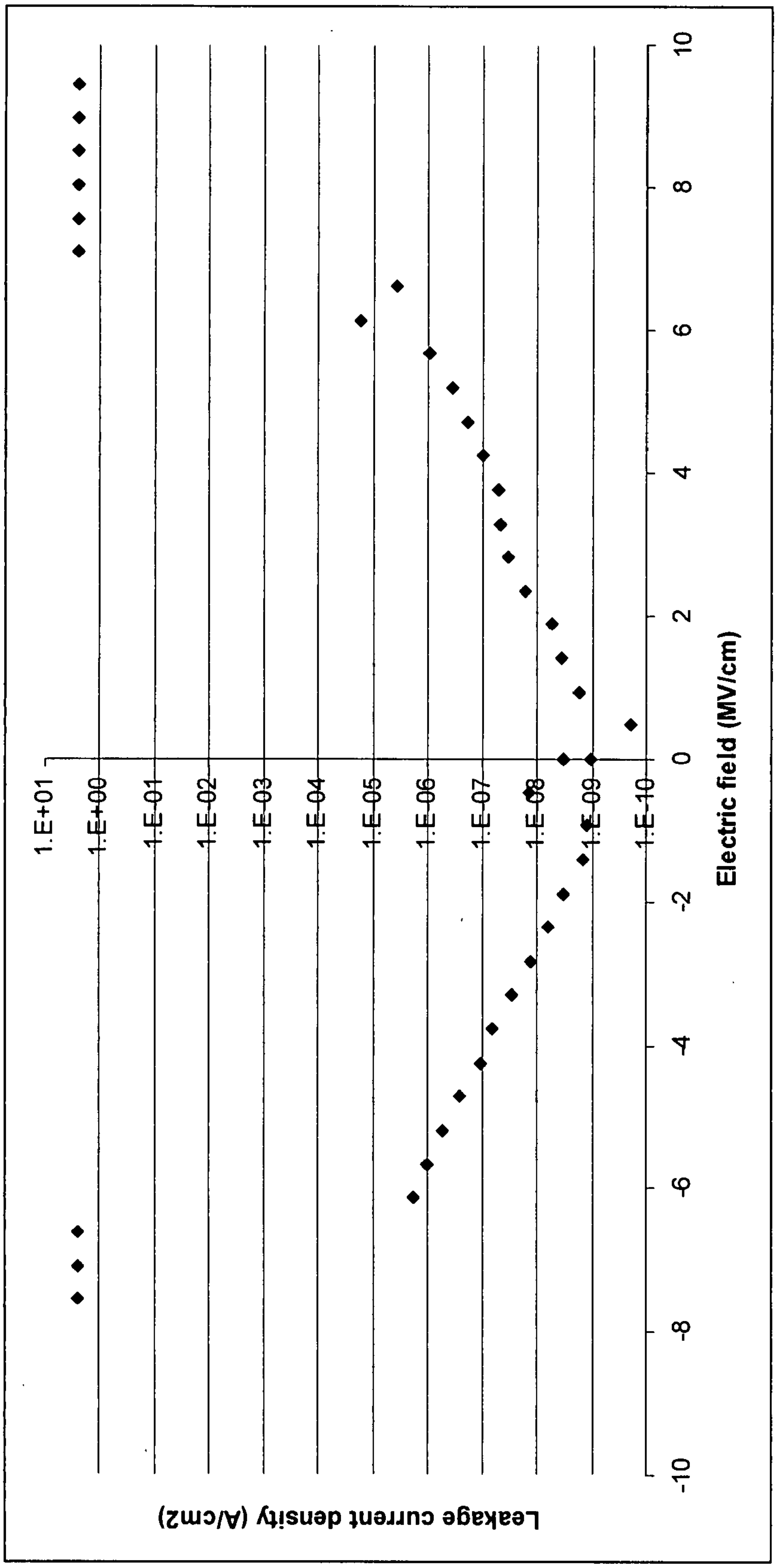

Leakage current density (A/cm2)
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
1.E-07
1.E-08
1.E-09
1.E-10
-10
-8
-6
-4
-2
0
2
4
6
8
10
Electric field (MV/cm)

Figure 13

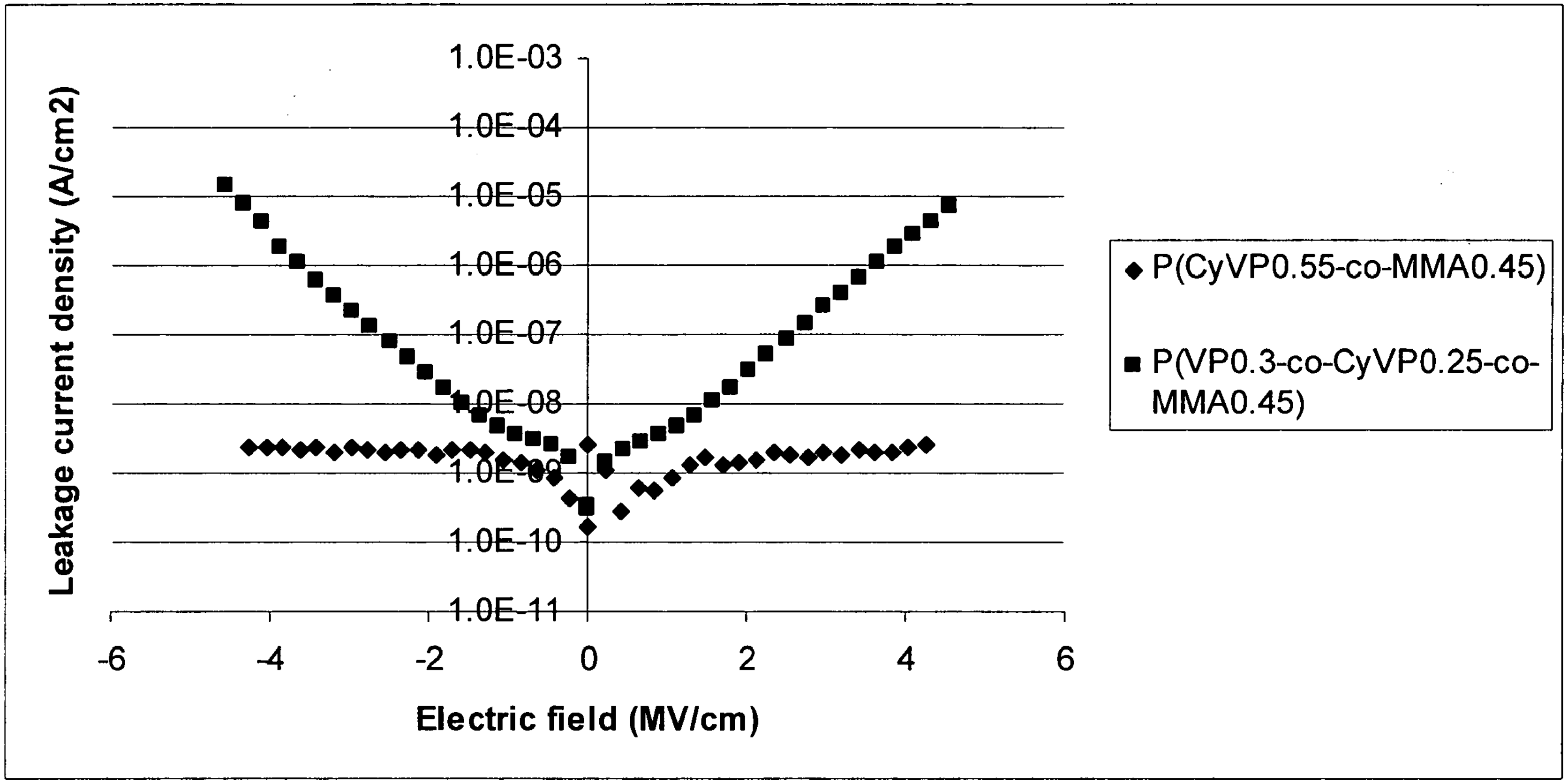

Leakage current density (A/cm2)
1.0E-03
1.0E-04
1.0E-05
1.0E-06
1.0E-07
1.0E-08
1.0E-09
1.0E-10
1.0E-11
-6
-4
-2
0
2
4
6
Electric field (MV/cm)
◆ P(CyVP0.55-co-MMA0.45)
■ P(VP0.3-co-CyVP0.25-co-MMA0.45)

Figure 14

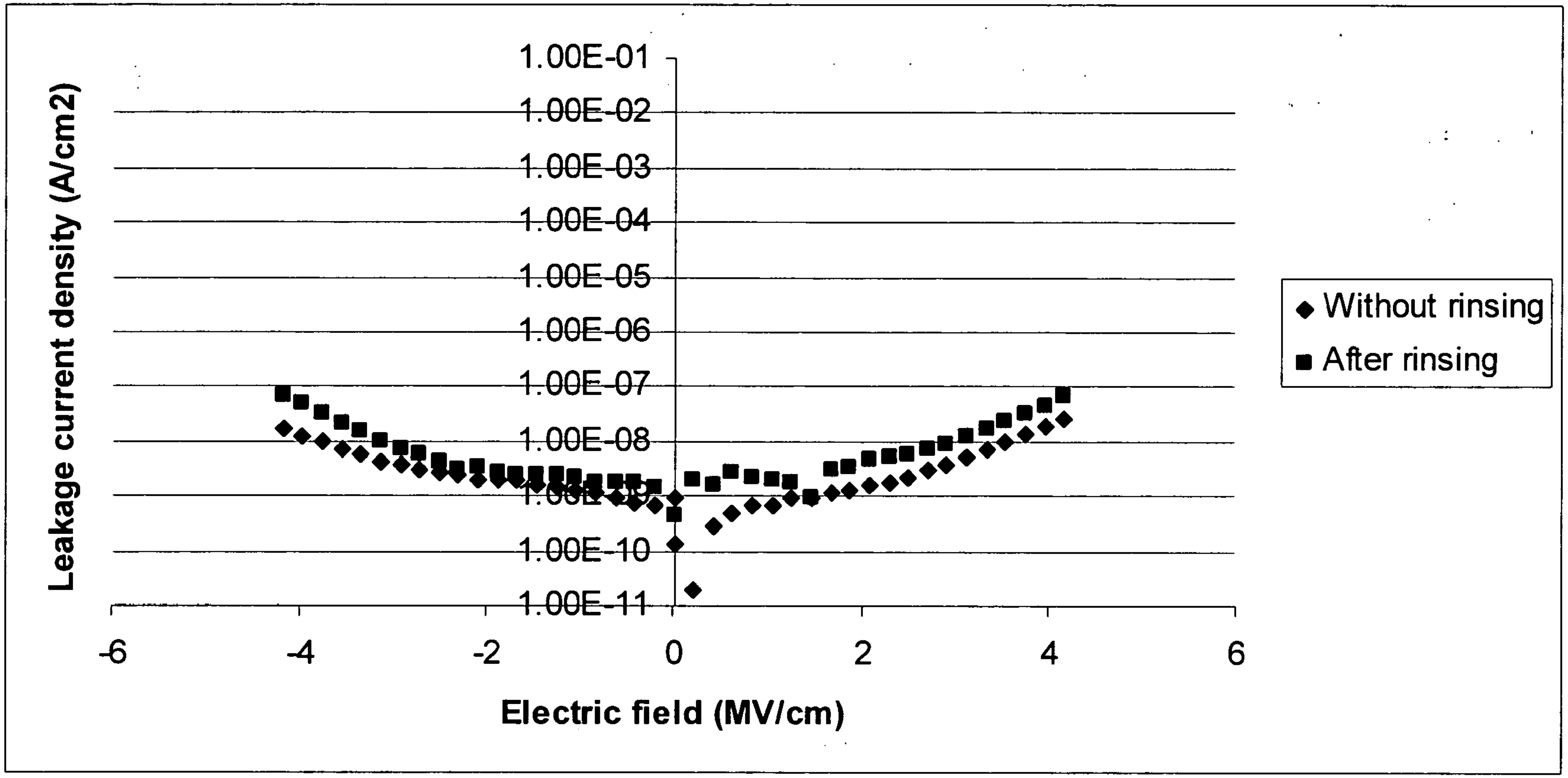

1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
1.00E-09
1.00E-10
1.00E-11
Leakage current density (A/cm2)
-6
-4
-2
0
2
4
6
Electric field (MV/cm)
◆ Without rinsing
■ After rinsing

Figure 15

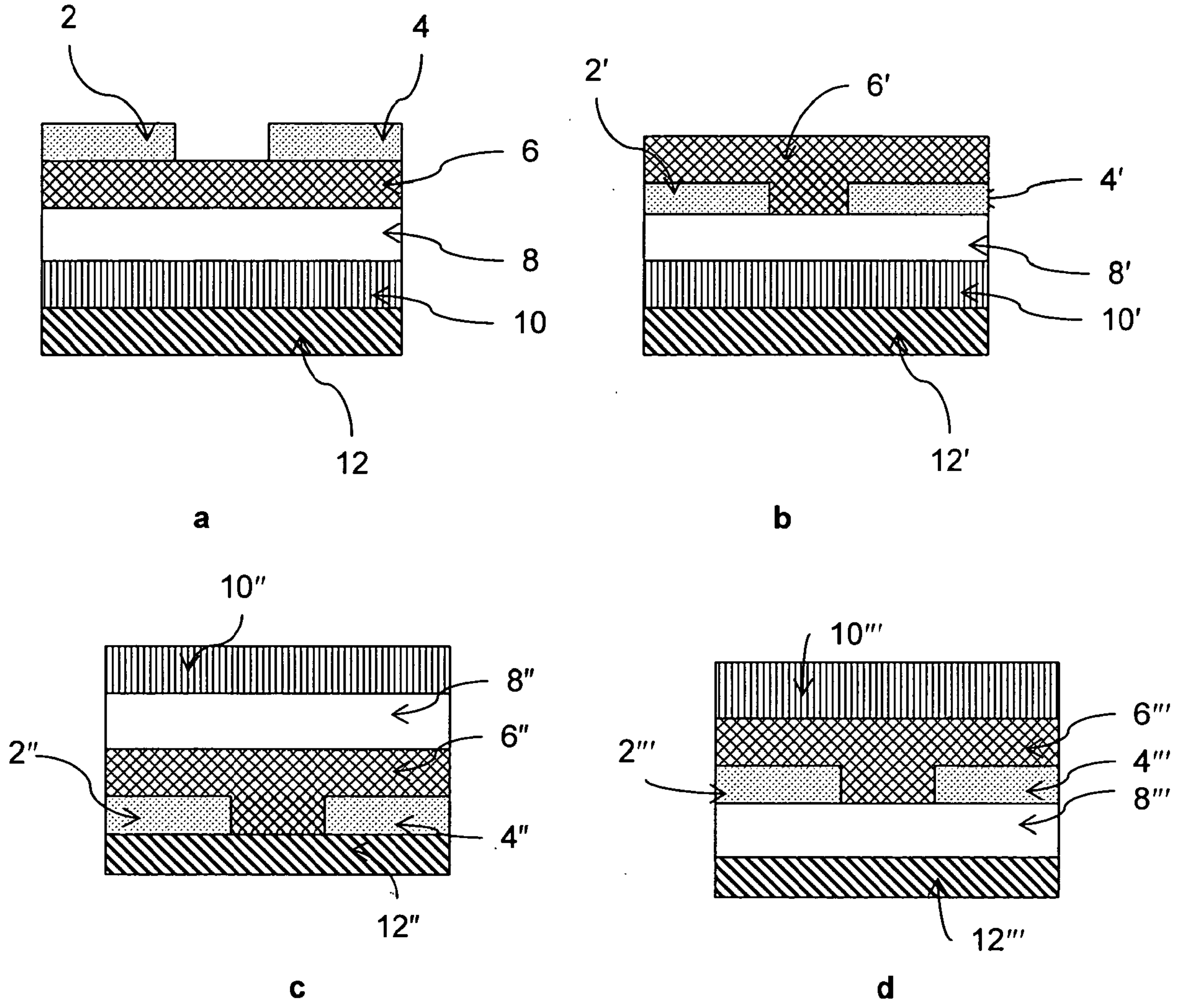
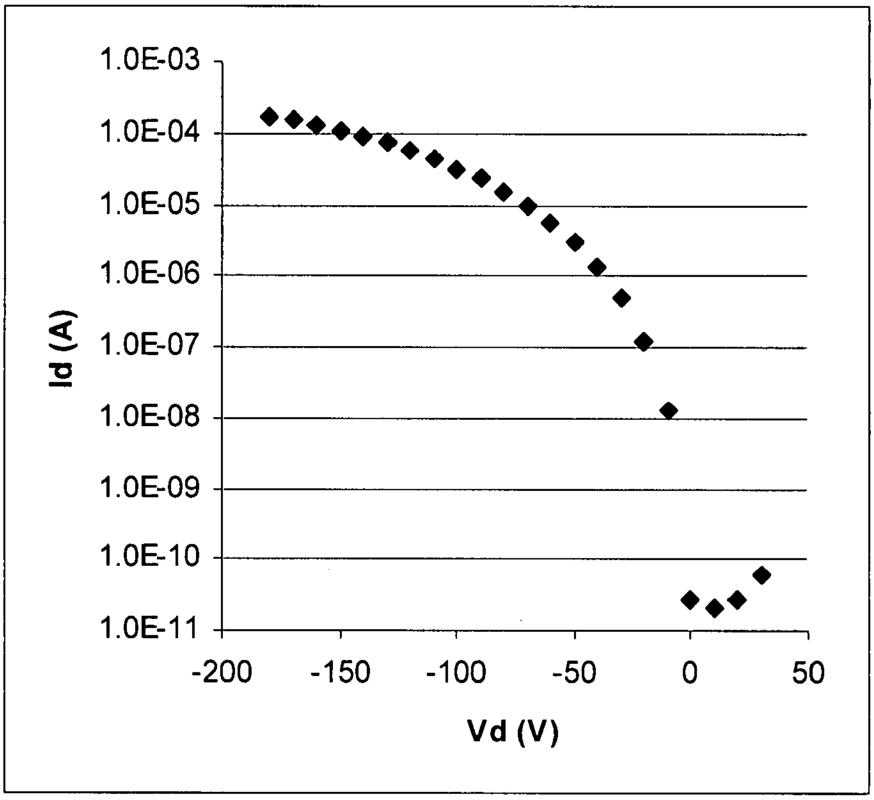
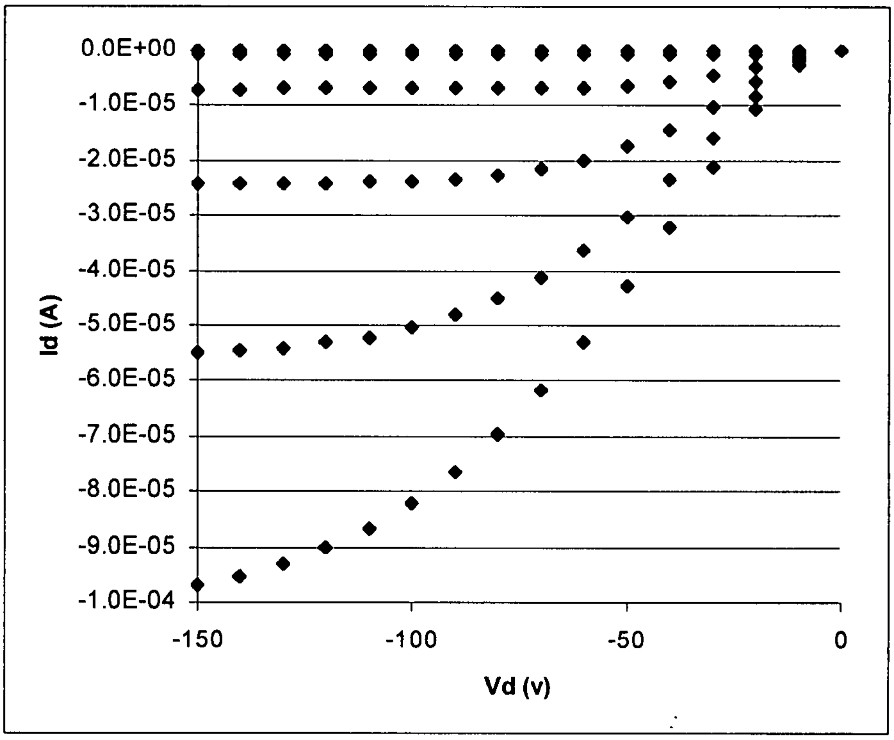


Figure 16



Transfer plot



Output plot

Figure 17

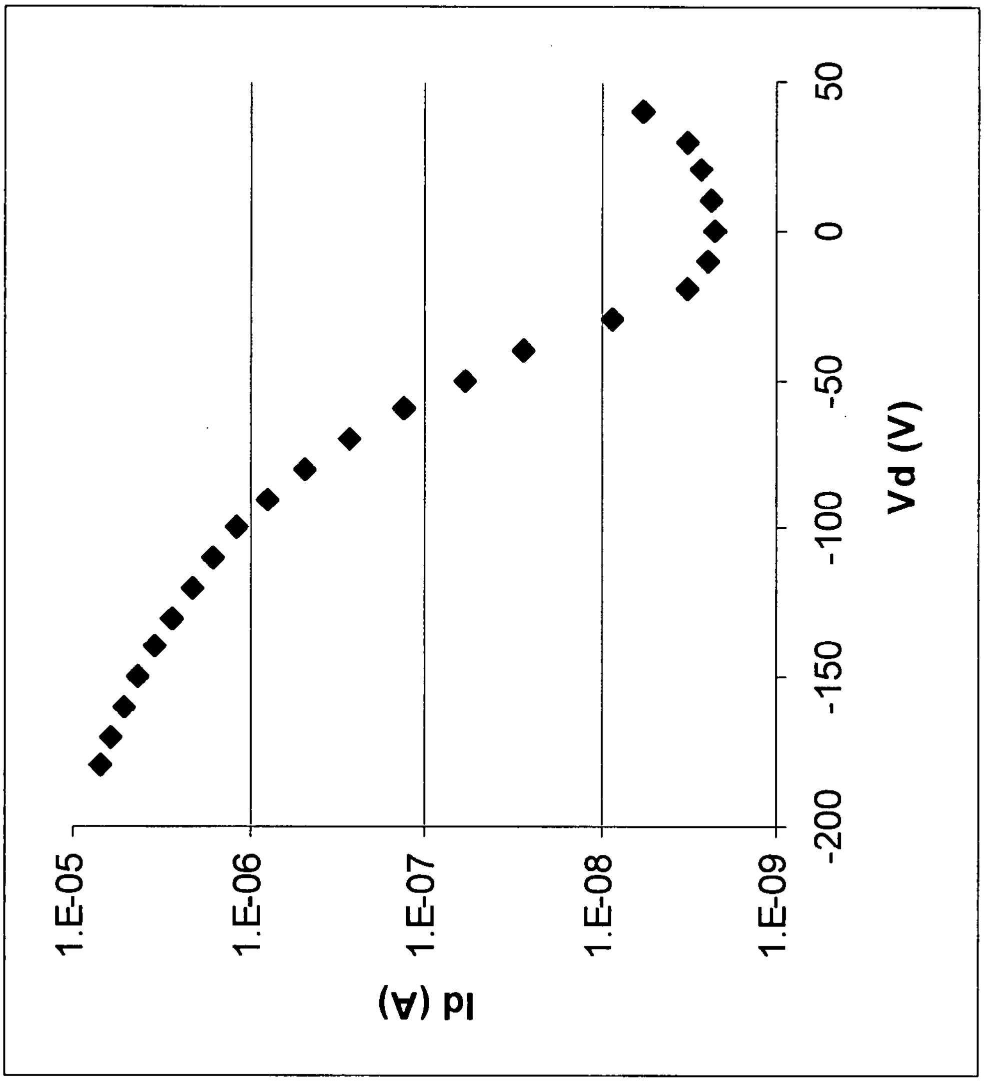


Figure 18

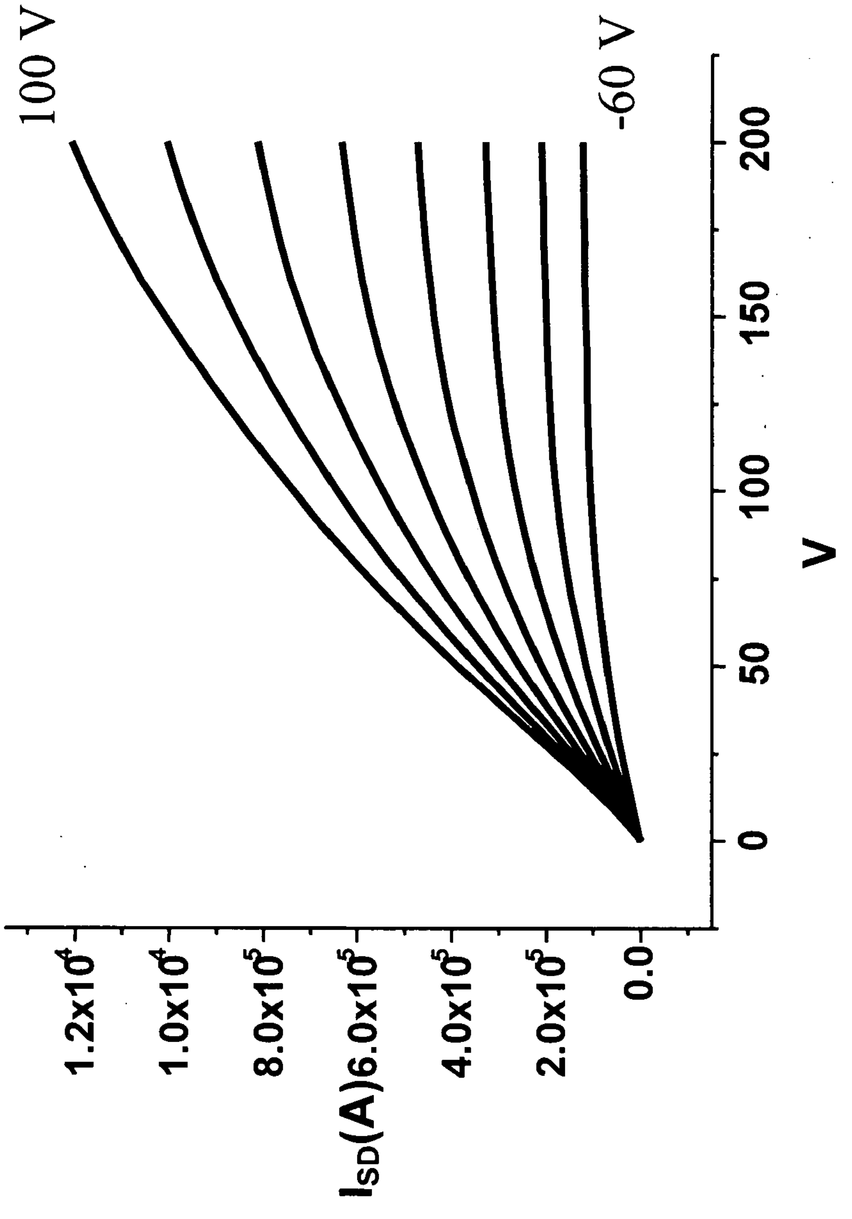

100 V
-60 V
I_{SD}(A)
1.2x10^{4}
1.0x10^{4}
8.0x10^{5}
6.0x10^{5}
4.0x10^{5}
2.0x10^{5}
0.0
0
50
100
150
200
V

Figure 19

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2007/024473

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F220/10

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)
C08F

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 517 746 A (FUJI PHOTO FILM CO LTD) 12 July 1978 (1978-07-12) page 5, line 12 - line 13 -----	1-7
A	US 6 458 310 B1 (LIU GUOJUN [CA]) 1 October 2002 (2002-10-01) column 7, line 60 - line 64 -----	1-39
A	EP 1 541 118 A (OREAL [FR]) 15 June 2005 (2005-06-15) claim 13 ----- -/--	1-39

☒ 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 document but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 24 April 2008	Date of mailing of the international search report 06/05/2008
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Rouault, Yannick

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DING J ET AL: "POLYISOPRENE-BLOCK-POLY(2-CINNAMOYLETHYL METHACRYLATE) VESICLES ANDTHEIR AGGREGATES" MACROMOLECULES, ACS, WASHINGTON, DC, US, vol. 30, no. 3, 10 February 1997 (1997-02-10), pages 655-657, XP000678017 ISSN: 0024-9297 the whole document	1-39
A	DING J ET AL: "POLYSTYRENE-BLOCK-POLY(2-CINNAMOYLETHYL METHACRYLATE) NANOSPHERES WITH CROSS-LINKED SHELLS" MACROMOLECULES, ACS, WASHINGTON, DC, US, vol. 31, no. 19, 22 September 1998 (1998-09-22), pages 6554-6558, XP000778174 ISSN: 0024-9297 the whole document	1-39
A	HENSELWOOD F ET AL: "WATER-SOLUBLE POROUS NANOSPHERES" MACROMOLECULES, ACS, WASHINGTON, DC, US, vol. 31, no. 13, 30 June 1998 (1998-06-30), pages 4213-4217, XP000765438 ISSN: 0024-9297 the whole document	1-39
A	XIA S J ET AL: "Properties of thin polystyrene-poly(2-cinnamoylethyl methacrylate) (PS-PCEMA) copolymeric coatings on gold electrodes" ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 46, no. 4, 1 December 2000 (2000-12-01), pages 475-485, XP004225096 ISSN: 0013-4686 the whole document	1-39
A	XIA S J ET AL: "Electrochemical characteristics of dip-coated poly (2-cinnamoylethyl methacrylate) (PCEMA) films on Au surfaces" ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 46, no. 4, 1 December 2000 (2000-12-01), pages 463-474, XP004225095 ISSN: 0013-4686 the whole document	1-39

-/--

International application No
PCT/US2007/024473

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LIU G ET AL: "DIBLOCK THIN FILMS WITH REGULARLY PACKED NANOCHANNELS" POLYMER PREPRINTS, AMERICAN CHEMICAL SOCIETY, US, vol. 40, no. 2, 1990, pages 982-983, XP008034720 ISSN: 0032-3934 the whole document -----	1-39

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2007/024473

Box No. II **Observations where certain claims were found unsearchable (Continuation of item 2 of 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. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims 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:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent 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:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an 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 reportcovers only those claims for which fees were paid, specifically claims 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 claims 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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: -

The present claims relate to an extremely large number of possible compounds. Support and disclosure in the sense of Article 6 and 5 PCT is to be found however for only a very small proportion of the compounds claimed, see the examples. The non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of the claims (PCT Guidelines 9.19 and 9.23).

The search of the claims was restricted to those claimed compounds which appear to be supported by the examples.

The present claims relate to a compound which has a given desired property or effect, namely leakage current density . However, the description does not provide support and disclosure in the sense of Article 6 and 5 PCT for any such compound having the said property or effect and there is no common general knowledge of this kind available to the person skilled in the art. This non-compliance with the substantive provisions is to such an extent, that the search was performed taking into consideration the non-compliance in determining the extent of the search of the claim (PCT Guidelines 9.19 and 9.20).

The search of the claims was consequently restricted to the specifically disclosed compound having the desired property or effect.

Particularly, PCyVP in example 1, a product known in the art (see GB1517746) belongs to the set of claimed compounds but has not the expected properties (see Table 1) and has not been searched.
The same applies for P(VP0.3-co-CyVP0.25-co-MMA0.45) in example 4.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2007/024473

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
GB 1517746	A	12-07-1978	DE	2540561	A1	01-04-1976
			FR	2284902	A1	09-04-1976
			JP	1144279	C	26-04-1983
			JP	51034007	A	23-03-1976
			JP	56012518	B	23-03-1981
US 6458310	B1	01-10-2002	NONE			
EP 1541118	A	15-06-2005	AT	352286	T	15-02-2007
			CA	2487637	A1	11-06-2005
			DE	602004004486	T2	08-11-2007
			ES	2276253	T3	16-06-2007
			FR	2863485	A1	17-06-2005
			JP	2005187475	A	14-07-2005