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(54) Title: UV CURE COATINGS FOR MEDICAL DEVICES

(57) Abstract: The invention concerns hydrophobic and hydrophilic coating compositions for medical devices or medical implants. The hydrophilic coating composition comprises a polymer which is soluble in water or water-alcohol solutions, the polymer made from monomers comprising: (a) at least one monomer that is a photo radical generator, and (b) at least one monomer comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides: wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator group is 20:1 to 500:1. This hydrophilic coating composition can provide the entire coating or, with a hydrophobic basecoat, can be the topcoat of a 2 coat system.

UV CURE COATINGS FOR MEDICAL DEVICES

TECHNICAL FIELD

[0001] The invention concerns ultraviolet light curable coatings for medical devices and implants.

BACKGROUND

[0002] The present invention relates to the field of non-thrombogenic and lubricious coatings that are applied to medical devices, especially devices intended to be implanted, temporarily or permanently, in the body and in blood-contact applications.

[0003] Among the many advances in medical practice in recent years is the development of medical devices that supplement the surgeon's skills. Examples of these are a variety of vascular catheters and guide wires that can be used to treat remote areas of the circulatory system otherwise available only by major surgery. Another is the stent, a device that reinforces arterial walls and prevents occlusion after angioplasty. Another is the intra-ocular lens that restores youthful eyesight to the elderly afflicted with cataracts. Heart valves, artificial pacemakers, and orthopedic implants are among a lengthening list of other such devices.

[0004] Nearly all of the above-described devices are constructed of plastics and metals that were never intended to invade and sometimes reside for prolonged periods in the human body. They present surfaces that bear little or no resemblance to those of human organs, which are generally hydrophilic, slippery and biocompatible.

[0005] Equally important for devices that must be inserted and moved through body tissues is their lubricity. Most metals and plastics have poor lubricity against body tissues, which results in mechanical abrasion and discomfort when the device is passed over the tissue.

[0006] The surfaces of devices designed and manufactured from such materials can be made biocompatible, as well as hydrophilic and slippery, by properly designed coatings. Thus, the way has been opened to construct medical devices from conventional plastics and metals having the particular physical properties required, and then to apply suitable coatings to impart the desired properties to their surfaces.

[0007] It has been shown that polymers that have low coefficients of friction when wet are water soluble polymers that are cross-linked or otherwise immobilized and swell, but

do not dissolve, upon exposure to water. Polysaccharides have been shown to be useful in making hydrophilic, lubricious coatings on substrates. Such coatings are described in U.S. Pat. Nos. 4,801,475, 5,023,114, 5,037,677, and 6,673,453, the disclosures of which are hereby incorporated by reference. Lubricious coatings based upon polysaccharides exhibit exceptional biocompatibility and lubricity, but relatively poor resistance to ionizing radiation.

[0008] It is desirable for some applications to have a lubricious coating made of a synthetic polymer for the benefits of a longer shelf-life and stability to radiation-sterilization processes. Hydrophilic synthetic polymers, such as poly(acrylic acid) and its copolymers have often been proposed to make lubricious, hydrophilic coatings because of their ability to generate a hydrated layer on the surface.

[0009] Many attempts have been made to immobilize poly(acrylic acid) on surfaces so that they may be utilized as coatings on medical devices. The methods in U.S. Pat. Nos. 4,642,267 and 4,990,357 include physical blends of poly(acrylic acid) copolymer with a polyurethane dispersion. This method has the drawback that the interpolymer network physically attaching the hydrophilic polymer to the substrate surface often breaks down upon prolonged turbulent flow or soaking and the hydrophilic species may be washed away thereby rendering the article insufficiently lubricious.

[0010] Other methods invented to utilize poly(acrylic acid) as a hydrophilic coating on a surface include radiation grafting of a carboxylic acid monomer and its polymer as described in U.S. Pat. Nos. 2,999,056, 5,531,715, 5,789,018, and 6,221,061, and EP 0669837, plasma grafting of an acrylic acid monomer in EP 0220919, and also methods using a primer layer containing isocyanate, aziridine, amine and hydroxyl functional groups to anchor polyacrylic acid as stated in U.S. Pat. Nos. 5,091,205, 5,509,899, 5,702,754, 6,048,620, 6,558,798, 6,709,706, 6,087,416, 6,534,559, and EP 0379156, EP 0480809, EP 0728487, and EP 0963761. The disclosures of all the above-mentioned patents are hereby incorporated by reference.

[0011] The above-mentioned poly(acrylic acid) coatings exhibit relatively poor lubricity and/or durability because of insufficient hydrophilic polymer coating thickness and/or poor binding to the surface. It is difficult to achieve a high-density surface coverage by either grafting through photo-initiated polymerization or surface chemical attachment of polymers. Multiple-repeated coating processes may increase the thickness of photo-initiated polymerization coating, but will greatly decrease productivity and add to the cost of manufacturing.

[0012] Using a cross-linker can increase the thickness of a hydrophilic coating considerably. The prior art includes methods to cross-link polyacrylic acid coatings by photo radiation and by the reaction of polyfunctional reactive compounds, such as melamine and aziridines, as described in U.S. Pat. Nos. 5,531,715, 6,558,798, and EP 533821. However, the cross-linked hydrophilic coatings in the art often face a trade-off between lubricity and abrasion resistance, which are both indispensable properties for a hydrophilic coating. A highly cross-linked coating has poor lubricity because of its low capacity for hydration and reduced mobility of polymer segments in aqueous media. A coating with a low cross-linking density has a high swelling ratio, which generally leads to poor abrasion resistance and weak mechanical strength.

[0013] U.S. Patent Application Pub. No. 2011/0200828 teaches a bilaminar coating that includes a basecoat that firmly adheres to the substrate and a topcoat that is chemically grafted to the basecoat. The topcoat comprises a mixture of a water-soluble polymer containing carboxylic acid groups and a water-soluble chromium (III) compound. The coating forms a very durable, lubricious layer when wet. However, the carboxylate anion comprising the coating shows poor performance in thrombogenicity tests, such as the partial thromboplastin time (PTT) test. The disclosure of the above-cited reference is hereby incorporated by reference.

[0014] Contacting blood with a foreign object having a plastic or metal surface induces a complex set of clot-forming reactions that occur at the blood surface interface. Thromboembolism is a major complication associated with the clinical use of artificial devices, such as catheters, guidewires, mechanical heart valves, ventricular assist devices, implantable artificial hearts, vascular grafts, *etc*. In particular, thromboembolism is an important complication of angiographic procedures, particularly with catheter and guidewire manipulations proximal to the brachiocephalic vessels.

[0015] Surface modification is commonly used to make the materials more blood-compatible, while minimizing any loss of mechanical properties. Two approaches to modification have been commonly used. Suppression of nonspecific protein adsorption using coatings of polyethylene oxide (PEO) (a neutral, hydrophilic, and highly flexible polymer) or other hydrophilic polymers has been investigated for surface passivation. Uncontrolled, nonspecific protein adsorption, which usually occurs within seconds following the exposure of a foreign surface to blood, can initiate blood coagulation and the complement pathways.

[0016] A second approach has been to use coatings that actively assist the anticoagulant activity of surfaces. Certain plasma proteins (such as antithrombin (AT) which

can inhibit thrombin and factor Xa (FXa)) or heparin (a glycosaminoglycan which catalyzes the reactions of plasma AT) have been used for this purpose. Frech *et al.*, in "A Simple Noninvasive Technique to Test Nonthrombogenic Surfaces," The American Journal of Roentgenology, vol. 113 (1971), p. 765-768, discloses coating of a guidewire with a benzalkonium-heparin complex. Ovitt *et al.*, in "Guidewire Thrombogenicity and Its Reduction", Radiology, vol. 111 (1974), p. 43-46, reports Teflon coated guidewires treated with benzalkoniumheparin. U.S. Pat. No. 4,349,467 (William) shows the application of heparin to solid polymeric resin substrates by steeping the substrate in a solution of ammonium salt and contacting the substrate with a heparin salt solution.

[0017] There have also been many attempts to invent hydrophilic polymers with applications ranging from electrophoresis, hair treatment and paper treatment. As revealed by Albarghouthi et al, in "Poly-N-hydroxyethylacrylamide(polyDuramide): A novel, hydrophilic, self-coating polymer matrix for DNA sequencing by capillary electrophoresis", Electrophoresis, vol. 23 (2002), p. 1429-1440, non-ionic monomers, such as N-hydroxyethyl acrylamide, have great hydrophilicity.

[0018] The following references, namely WO10041527A, W010041530A, W011125713A, JP2011046619A, JP2011046652A, JP2010126482A, and JP2010090049A, teach copolymers comprised of a 5-30 mol % of a carboxylic acid monomer and 70-95 mol % of an alcohol containing acrylic monomer for use in hair treatment formulations. These patent applications do not disclose the utility of the copolymers as lubricious, biocompatible coatings nor do they disclose their resistance to ionizing radiation. JP2006176934A teaches copolymers from methacrylamide, hydroxyethyl acrylamide, and an ionic vinyl monomer for use as an additive to increase the strength of the paper. The latter reference does not disclose the utility of the copolymers as lubricious, biocompatible coatings nor does it disclose their resistance to ionizing radiation.

[0019] There is a need for improved lubricious, biocompatible coatings that are resistant to ionizing radiation.

[0020] Typically, a basecoat resides between the substrate and the lubricious coating in a medical device or implant. The basecoat can improve stability of the lubricious coating. There is a need in the art for improved basecoats, such as ones that provide a more rapid binding of the lubricious topcoat. A basecoat that binds to the hydrophilic topcoat through ultraviolet (UV) cure would meet this need.

SUMMARY

[0021] The invention concerns coating compositions for medical devices or medical implants. These novel compositions include hydrophobic basecoat polymers and hydrophilic topcoat polymer.

[0022] In some embodiments, the invention concerns coating compositions comprising hydrophobic polymers for use as a photoreactive basecoat for a medical device or implant comprising a polymer made from monomers comprising:

(a) 1 to 12 mol % of at least one photoactive monomer that is a hydrogen atom abstracter and

(b) 99 to 88 mol % of one or more of acrylamides, methacrylamides, acrylates, methacrylates, and N-vinylpyrrolidone; wherein the polymer has a glass transition temperature (Tg) of less than 40 °C.

[0023] In certain embodiments, the basecoats additionally comprise a multifunctional aziridine. (a) 95-99.8 wt % of the hydrophobic polymer described herein; and (b) 0.2- 5 wt % multifunctional aziridine based on the total weight of the basecoat.

[0024] The invention also concerns medical devices or implants comprising a photoreactive basecoat comprising a coating composition described herein. In preferred composition, the basecoat is hydrophobic. In some embodiments, the device or implant contains a hydrophilic topcoat where the basecoat resides on a substrate and the topcoat resides on the basecoat. The hydrophilic topcoat composition may comprise, but need not comprise, photoactive groups.

[0025] In other embodiments, the invention concerns coating solutions comprising a hydrophobic basecoat coating composition described herein and a solvent.

[0026] In other embodiments the coating solution comprises a polymer which is soluble in water or water-alcohol solutions, the polymer made from monomers comprising: (a) at least one monomer that is a photo radical generator, and (b) at least one monomer comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides; wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator group is 20:1 to 500:1.

[0027] The invention also concerns coated substrates comprising a substrate and a lubricious coating made using a coating composition described herein.

[0028] Additional embodiments concern coating a composition described herein in an aqueous solution.

[0029] In yet another embodiment, the invention concerns method of coating substrates. In some embodiments, both a basecoat and a topcoat are applied to a substrate. When both the basecoat and the topcoat are cured by UV light, either (a) the basecoat is applied and cured before the topcoat is added or (b) the basecoat is applied and dried, the topcoat is added and, then, both the basecoat and topcoat are cured by UV light.

[0030] Yet other embodiments include medical devices or implants where a lubricious coating contains a pharmaceutical or antimicrobial agent blended with the coating composition.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0031] The requirements for any coating intended for use on medical devices will be set forth and explained first. The specification will then show how the present invention fulfills these requirements.

[0032] The coatings of the instant invention are suitable for use in medical devices. The coating of the present invention has the following properties:

(1) the coating must be able, on drying, to form a continuous, adherent film of good integrity on the surface of the material to be coated. This means that the minimum film-forming temperature of the coating solution must be lower than the expected drying temperature to be used during device fabrication;

(2) the formed polymer film must be flexible and adherent enough to conform without rupture to the bending and twisting of the coated device under the expected conditions of use;

(3) when the coated device is immersed for long periods in aqueous media such as human blood, the film must not weaken or lose its integrity;

(4) the coating must present a non-cytotoxic and blood compatible surface. When contacted with human blood the coating must not initiate blood coagulation and the complement pathways;

(5) the coating must be firmly and securely bound to the substrate so that no particles or fragments or leachable components can contaminate an aqueous medium such as human blood; and

(6) the coating must withstand some acceptable form of sterilization without loss of integrity, durability, or biocompatibility.

[0033] A coating which satisfies the above requirements is made as described below.

[0034] The present disclosure may be understood more readily by reference to the following description taken in connection with the accompanying Figures and Examples, all of which form a part of this disclosure. It is to be understood that this disclosure is not limited to the specific products, methods, conditions or parameters described and/ or shown herein, and that the terminology used herein is for the purpose of describing particular embodiments by way of example only and is not intended to be limiting of any claimed disclosure. Similarly, unless specifically otherwise stated, any description as to a possible mechanism or mode of action or reason for improvement is meant to be illustrative only, and the invention herein is not to be constrained by the correctness or incorrectness of any such suggested mechanism or mode of action or reason for improvement. Throughout this text, it is recognized that the descriptions refer both to methods of operating a device and systems and to the devices and systems providing said methods. That is, where the disclosure describes and/or claims a coating composition, medical device, coating solution or method, it is appreciated that these descriptions and/or claims also describe and/or claim the devices, equipment, or systems for accomplishing these methods.

[0035] In some embodiments, the invention concerns coating compositions comprising hydrophobic polymer for use as a photoreactive basecoat for a medical device or implant comprising a polymer made from monomers comprising:

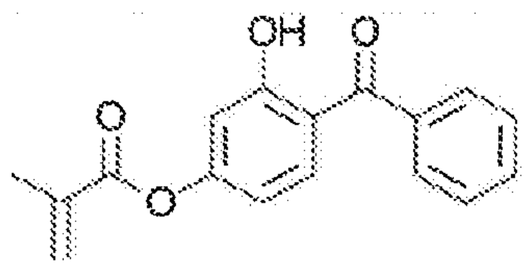
(a) 1 to 12 mol % of at least one photoactive monomer that is a hydrogen atom abstracter and

(b) 99 to 88 mol % of one or more of acrylamides, methacrylamides, acrylates, methacrylates, and N-vinylpyrrolidone; wherein the hydrophobic polymer has a glass transition temperature (Tg) of less than 40 ºC.

[0036] Preferred hydrophobic polymers have a glass transition temperature of less than 40 ºC, 20 ºC, 15 ºC or 10 ºC.

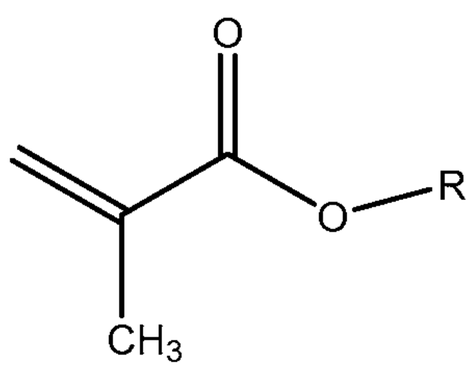
[0037] In preferred embodiments of the hydrophobic polymer, the photoactive monomer that is a hydrogen atom abstracter is a benzophenone compound. In certain embodiments, the photoactive monomer that is a hydrogen atom abstracter comprises one or more of 4-methacryloxy-2-hydroxybenzophenone, 4-acryloxybenzophenone, 4-methacryloxybenzophenone, acrylamidobenzophenone, methacrylamidobenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone, and 2-hydroxy-4-methacryloxyethoxybenzophenone.

[0038] 4-Methacryloxy-2-hydroxy benzophenone (MHB) can be copolymerized with (meth)acrylate monomers to produce a hydrophobic, photoactive polymer. Upon UV cure this polymer functions as a tie layer to bind the substrate to a hydrophilic topcoat layer. Topcoats cured in the presence of this photoactive basecoat bind well even if the topcoat contains no photoactive component.



4-methacryloxy-2-hydroxy benzophenone (MHB)

[0039] The monomers copolymerized with the photoactive monomer may be one or more acrylate, methacrylate, or other monomers known to copolymerize well with them. In certain embodiments, the polymer comprises methacrylate of the structure



where R is an optionally substituted C_1-C_{20} alkyl. In some embodiments, R may be methyl, ethyl, or butyl. Preferably the copolymer will contain monomers such as ethylhexyl, isodecyl, dodecyl or others that contribute to a low glass temperature copolymer. The copolymer also contains monomers with some hydrophilic character to provide good interaction with the topcoat solution and polymer. Examples include hydroxyethyl methacrylate and N-vinylpyrrolidone monomers.

[0040] In certain embodiments, the monomer contributing low glass temperature to the hydrophobic polymer is an acrylate having a C_4-C_{20} alkyl group, such as butyl acrylate.

[0041] In yet other aspects, the invention concerns coating solutions comprising 2 to 15 wt% of a hydrophobic polymer coating composition described herein. In other embodiments, the solution comprises 3 to 13 wt% or 4 to 12 wt% or 5 to 10 wt% of a coating composition described herein. In preferred embodiments, the solution comprises an organic solvent. Preferred solvents include one or more of toluene, ethanol, acetone, isopropanol, ethyl acetate, dimethylformamide, tetrahydrofuran, butanol, N-methyl-2-pyrrolidone, n-butyl

acetate, 1,2-propanediol monomethyl ether acetate, isobutyl acetate, isopropyl acetate, methyl acetate, 3-methyl-1-butanol, methylethyl ketone, 2-methyl-1-propanol, 1-pentanol, 2-propanol, propyl acetate, dichloromethane, dimethyl sulfoxide, methylbutyl ketone and xylene.

[0042] In certain embodiments, the basecoat additionally comprises a multifunctional aziridine. In some embodiments, the coating composition comprises (a) 95-99.8 wt % of the hydrophobic polymer; and (b) 0.2- 5 wt % multifunctional aziridine. In other embodiments, the coating composition comprises (a) 98-99.5 wt % of the hydrophobic polymer; and (b) 0.5- 2 wt % multifunctional aziridine.

[0043] In some embodiments, the invention concerns hydrophilic polymer coating compositions for medical devices or medical implants comprising a polymer which is soluble in water or water-alcohol solutions, the polymer made from monomers comprising:

(a) at least one monomer that is a photo radical generator, and

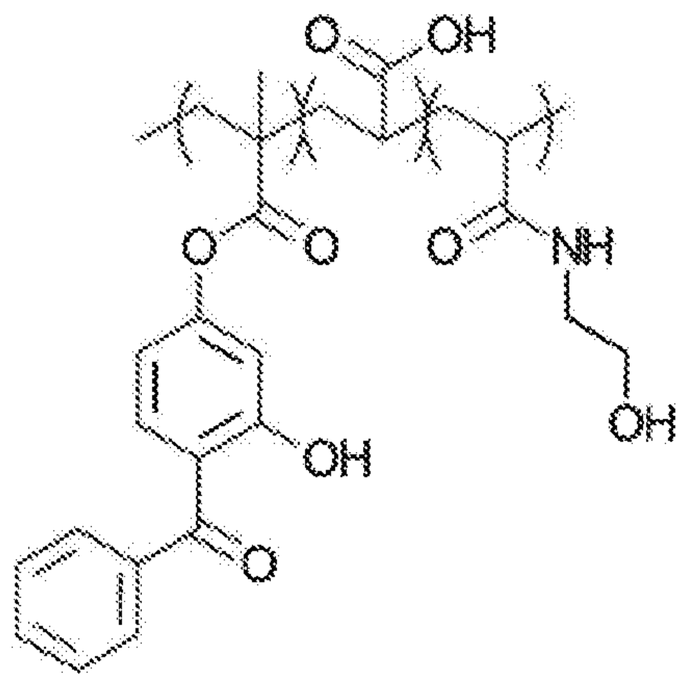
(b) at least one monomer comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides;

wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator group is 20:1 to 500:1.

[0044] The polymer may be packaged in a water or water-alcohol mixture. The alcohol is typically a C_1-C_6 alcohol. Preferred alcohols include methanol, ethanol and iso-propanol. The ratio of water to alcohol can be 100:0 to 50: 50.

[0045] Some preferred photo radical generators for the hydrophobic polymer are benzophenone compounds. In some embodiments, the photo radical generator comprises one or more of 4-methacryloxy-2-hydroxybenzophenone, 4-acryloxybenzophenone, 4-methacryloxybenzophenone, acrylamidobenzophenone, methacrylamidobenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone, 2,4-dihydroxy-4'-vinyl benzophenone, and 2-hydroxy-4-methacryloxyethoxybenzophenone. One preferred photo radical generator group comprises 4-methacryloxy-2-hydroxybenzophenone.

[0046] 4-Methacryloxy-2-hydroxy benzophenone (MHB) can be copolymerized with polar acrylates such as Acrylic Acid and N-(2-Hydroxyethyl)acrylamide to produce a hydrophilic, photoactive polymer. Upon UV cure this polymer functions as a lubricious topcoat. It can also be used as an additive to other hydrophilic (non-photoactive) polymers to form a lubricious coating after UV Cure.



Random copolymer of MHB, Acrylic Acid, and N-(2-Hydroxyethyl)acrylamide

[0047] A variety of ethylenic monomers may be used to form the hydrophilic polymer. In some embodiments the monomers comprise at least one acidic group comprises acrylic acid, methacrylic acid, 2-ethylacrylic acid, 2-propylacrylic acid, acryloxypropionic acid, isocrotonic acid, maleic anhydride, maleic acid and half esters, half amides and half thioesters of maleic acid, fumaric acid and itaconic acid, and mixtures thereof. In some embodiments, the ethylenic monomers comprise N-(2-hydroxyethyl)acrylamide and acrylic acid. In certain embodiments, the molar ratio of N-(2-hydroxyethyl)acrylamide to acrylic acid is 2:1 to 5:1.

[0048] Preferred acrylates and acrylamides include acrylamide, N-(2-hydroxyethyl)acrylamide, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, and N-(2-hydroxyethyl) methacrylamide, N-acryloylamido-ethoxyethanol, N-(hydroxymethyl) acrylamide, N-[tris(hydroxymethyl)methyl]acrylamide, 4-hydroxybutyl acrylate, hydroxypropyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, hydroxypropyl methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, 1,4-butanediol vinyl ether, di(ethylene glycol)vinyl ether, ethylene glycol vinyl ether, N,N-1,2-dihydroxyethylene-bis-acrylamide, N,N-1,2-dihydroxyethylene-bis-methyacrylamide, N-hydroxymethyl methacrylamide, N-tri(hydroxymethyl)-methyl-methacrylamide, or any mixture of the foregoing.

[0049] In some embodiments, the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator comprising at least one photopolymerizable group is 40:1 to 200:1.

[0050] In certain embodiments, the hydrophilic polymer has a weight-average molecular weight (Mw) of between 20,000 and 800,000 or 20,000 to 400,000 or 50,000 and 400,000.

[0051] Some hydrophilic polymer coating compositions additionally comprise a second polymer which is soluble in water or water-alcohol solutions. In some embodiments, the second polymer comprises one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides. In the second polymer, the ethylenic monomers of the second polymer comprise at least one acidic group, the ethylenic monomers of the second polymer comprising the at least one acidic group comprise one or more of acrylic acid, methacrylic acid, 2-ethylacrylic acid, 2-propylacrylic acid, acryloxypropionic acid, isocrotonic acid, maleic anhydride, maleic acid and half esters, half amides and half thioesters of maleic acid, fumaric acid, itaconic acid, and any combination thereof. Additionally, in the second polymer the acrylates or acrylamides comprise acrylamide, N-(2-hydroxyethyl)acrylamide, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, and N-(2-hydroxyethyl) methacrylamide, N-acryloylamido-ethoxyethanol, N-(hydroxymethyl) acrylamide, N-[tris(hydroxymethyl)methyl]acrylamide, 4-hydroxybutyl acrylate, hydroxypropyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, hydroxypropyl methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, 1,4-butanediol vinyl ether, di(ethylene glycol)vinyl ether, ethylene glycol vinyl ether, N,N-1,2-dihydroxyethylene-bis-acrylamide, N,N-1,2-dihydroxyethylene-bis-methyacrylamide, N-hydroxymethyl methacrylamide, N-tri(hydroxymethyl)-methyl-methacrylamide, and any mixture of the foregoing.

[0052] In some embodiments, the second polymer has a weight-average molecular weight (Mw) of between 50,000 and 800,000.

[0053] The invention also concerns coated substrates comprising a substrate and a lubricious coating made using a coating composition described herein. Preferred embodiments, additionally comprise a basecoat that contacts both the substrate and the lubricious coating composition. Preferred basecoats are hydrophobic.

[0054] The invention also concerns medical devices or implants comprising a photoreactive basecoat comprising a coating composition described herein. In some embodiments, the basecoat resides between a substrate and a hydrophilic topcoat. Some preferred topcoats comprise one or more of polyacrylate, polyvinylpyrrolidones, hyaluronic acid and polyacrylamide. In other embodiments, the topcoat comprises a N-(2-

hydroxyethyl)acrylamide and acrylic acid copolymer. Some embodiments comprise a plurality of covalent cross-links between said basecoat and said hydrophilic topcoat.

[0055] The coatings may be used on any medical device or implant suitable for the coating's application. In some embodiments, the substrate is plastic or metallic.

[0056] Preferred coated substrates have a lubricity of less than 25 gf friction and a durability of less than 50 gf friction as measured by a pinch test.

[0057] The invention also concerns medical devices and medical implants comprising a coated substrate described herein. In some embodiments, the medical device or medical implant is sterilized by at least one of gamma-ray, E-beam, and ethylene oxide.

[0058] In additional embodiments, the coatings described herein contain a pharmaceutical or antimicrobial agent blended with the coating composition.

[0059] Preferred medical devices include catheters or guide wires.

[0060] In some aspects, the invention concerns methods of coating articles. Some methods comprise coating a substrate with a basecoat comprising a coating composition described herein. The basecoat may be cured by exposure of the basecoat to UV light. In some embodiments, the basecoat may be coated with a hydrophilic topcoat.

[0061] In yet other embodiments, the coating methods include coating a substrate with a basecoat comprising a coating composition described herein, coating the basecoat with a hydrophilic topcoat and curing the basecoat and topcoat UV light. The hydrophilic topcoat can be photoactive (i.e. contain groups that absorb UV radiation and react when exposed to UV radiation), but the presence of photoactive groups in the topcoat is not necessary.

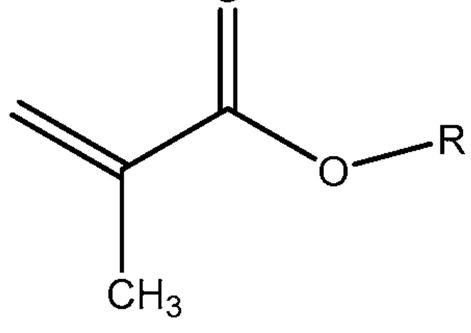
[0062] The invention relates at least to the following aspects.

[0063] Aspect 1A. A coating composition comprising hydrophobic polymer for use as a photoreactive basecoat for a medical device or implant comprising a polymer made from monomers comprising: (a) 1 to 12 mol % of at least one photoactive monomer that is a hydrogen atom abstracter, and (b) 99 to 88 mol % of one or more of acrylamides, methacrylamides, acrylates, methacrylates, and N-vinylpyrrolidone; wherein the polymer has a glass transition temperature (Tg) of less than 40 °C.

[0064] Aspect 1B. A coating composition comprising hydrophobic polymer for use as a photoreactive basecoat for a medical device or implant, the coating composition comprising a polymer made from monomers comprising: (a) 1 to 5 mol % of at least one photoactive monomer that is a hydrogen atom abstracter, and (b) 99 to 95 mol % of one or more of acrylamides, methacrylamides, acrylates, methacrylates, and N-vinylpyrrolidone; wherein the polymer has a glass transition temperature (Tg) of less than 40 °C.

[0065] Aspect 2. The coating composition of aspect 1A-1B, additionally comprising a multifunctional aziridine.

[0066] Aspect 3. The coating composition of aspect 2, comprising (a) 95-99.8 wt % of the hydrophobic polymer; and (b) 0.2-5 wt % multifunctional aziridine.

[0067] Aspect 4. The coating composition of anyone of aspects 1A-3, comprising methacrylate of the structure  where R is an optionally substituted C_1-C_{20} alkyl.

[0068] Aspect 5. The coating composition of aspect 4, wherein R is one or more of methyl, ethylhexyl, isodecyl, or dodecyl.

[0069] Aspect 6. The coating composition of aspect 4, wherein the hydrophobic polymer comprises hydroxyethyl methacrylate and N-vinylpyrrolidone.

[0070] Aspect 7. The coating composition of anyone of aspects 1A-6, wherein the hydrophobic polymer comprises acrylate having a C_4-C_{20} alkyl group.

[0071] Aspect 8. The coating composition of anyone of aspects 1A-7, wherein the photoactive monomer that is a hydrogen atom abstracter comprises a benzophenone moiety.

[0072] Aspect 9. The coating composition of aspect 8, wherein the photoactive monomer that is a hydrogen atom abstracter comprises one or more of 4-methacryloxy-2-hydroxybenzophenone, 4-acryloxybenzophenone, 4-methacryloxybenzophenone, acrylamidobenzophenone, methacrylamidobenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone, and 2-hydroxy-4-methacryloxyethoxybenzophenone.

[0073] Aspect 10. The coating composition of anyone of aspects 1A-9 having a Tg of less than 20 °C.

[0074] Aspect 11. A medical device or implant comprising a photoreactive basecoat comprising a coating composition of any one of aspects 1A-10.

[0075] Aspect 12. The medical device of aspect 11, wherein the basecoat resides between a substrate and a hydrophilic topcoat.

[0076] Aspect 13. The medical device of aspect 12, wherein the topcoat comprises one or more of polyacrylate, polyvinylpyrrolidones, hyaluronic acid and polyacrylamide.

[0077] Aspect 14. The medical device of aspect 12, wherein the topcoat comprises a N-(2-hydroxyethyl)acrylamide and acrylic acid copolymer.

[0078] Aspect 15. The medical device of aspect 11, wherein the medical device is a catheter or guide wire.

[0079] Aspect 16. The medical device of aspect 12, comprising a plurality of covalent cross-links between said basecoat and said hydrophilic topcoat.

[0080] Aspect 17. A coating solution comprising 2 to 15 wt% of a coating composition of any one of aspects 1-10 in a solvent.

[0081] Aspect 18. The coating solution of aspect17, wherein the solvent is an organic solvent.

[0082] Aspect 19. The coating solution of aspect 18, wherein the solvent comprises one or more of toluene, ethanol, acetone, isopropanol, ethyl acetate, dimethylformamide, tetrahydrofuran, butanol, N-methyl-2-pyrrolidon, n-butyl acetate, 1,2-propanediol monomethyl ether acetate, isobutyl acetate, isopropyl acetate, methyl acetate, 3-methyl-1-butanol, methylethyl ketone, 2-methyl-1-propanol, 1-pentanol, 2-propanol, propyl acetate, dichloromethane, dimethyl sulfoxide, methylbutyl ketone and xylene.

[0083] Aspect 20. A method of forming a coated article comprising coating a substrate with a basecoat comprising a coating composition of any one of aspects 1A-10.

[0084] Aspect 21. The method of aspect 20, additionally comprising curing the basecoat by exposure of the basecoat to UV light.

[0085] Aspect 22. The method of aspect 21, additionally comprising coating said basecoat with a hydrophilic topcoat.

[0086] Aspect 23. The method of aspect 20, additionally comprising (a) coating said basecoat with a hydrophilic topcoat and (b) curing the basecoat and topcoat with UV light.

[0087] Aspect 24. A coating composition for medical devices or medical implants comprising a polymer which is soluble in water or water-alcohol solutions, the polymer made from monomers comprising: (a) at least one monomer that is a photo radical generator comprising one or more of 4-methacryloxy-2-hydroxybenzophenone, 4-acryloxybenzophenone, 4-methacryloxybenzophenone, acrylamidobenzophenone, methacrylamidobenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone, 2,4-dihydroxy-4'-vinyl benzophenone, and 2-hydroxy-4-methacryloxyethoxybenzophenone, and (b) at least one monomer comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides; wherein the ethylenic

monomers comprise at least one acidic group comprises acrylic acid, methacrylic acid, 2-ethylacrylic acid, 2-propylacrylic acid, acryloxypropionic acid, isocrotonic acid, maleic anhydride, maleic acid and half esters, half amides and half thioesters of maleic acid, fumaric acid and itaconic acid, and mixtures thereof; wherein the acrylates or acrylamides comprise acrylamide, N-(2-hydroxyethyl)acrylamide, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, and N-(2-hydroxyethyl) methacrylamide, N-acryloylamido-ethoxyethanol, N-(hydroxymethyl) acrylamide, N-[tris(hydroxymethyl)methyl]acrylamide, 4-hydroxybutyl acrylate, hydroxypropyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, hydroxypropyl methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, 1,4-butanediol vinyl ether, di(ethylene glycol)vinyl ether, ethylene glycol vinyl ether, N,N-1,2-dihydroxyethylene-bis-acrylamide, N,N-1,2-dihydroxyethylene-bis-methyacrylamide, N-hydroxymethyl methacrylamide, N-tri(hydroxymethyl)-methyl-methacrylamide, or any mixture of the foregoing; wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator group is 20:1 to 500:1.

[0088] Aspect 25. The coating composition of aspect 24, wherein the photo radical generator group comprises 4-methacryloxy-2-hydroxybenzophenone.

[0089] Aspect 26. The coating composition of aspect 24, wherein the ethylenic monomers comprise N-(2-hydroxyethyl)acrylamide and acrylic acid.

[0090] Aspect 27. The coating composition of aspect 26, wherein the molar ratio of N-(2-hydroxyethyl)acrylamide to acrylic acid is 2:1 to 5:1.

[0091] Aspect 28. The coating composition of aspect 24, wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator comprising at least one photopolymerizable group is 40:1 to 200:1.

[0092] Aspect 29. The coating composition of aspect 24, wherein the polymer has a weight-average molecular weight (Mw) of between 20,000 and 800,000.

[0093] Aspect 30. The coating composition of aspect 24, additionally comprising a second polymer which is soluble in water or water-alcohol solutions.

[0094] Aspect 31. The coating composition of aspect 30, comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides.

[0095] Aspect 32. The coating composition of aspect 31, wherein the ethylenic monomers of the second polymer comprise at least one acidic group, the ethylenic monomers

of the second polymer comprising the at least one acidic group comprise one or more of acrylic acid, methacrylic acid, 2-ethylacrylic acid, 2-propylacrylic acid, acryloxypropionic acid, isocrotonic acid, maleic anhydride, maleic acid and half esters, half amides and half thioesters of maleic acid, fumaric acid, itaconic acid, and any combination thereof.

[0096] Aspect 33. The coating composition of aspect 31, wherein the acrylates or acrylamides of the second polymer comprise acrylamide, N-(2-hydroxyethyl)acrylamide, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, , and N-(2-hydroxyethyl) methacrylamide, N-acryloylamido-ethoxyethanol, N-(hydroxymethyl) acrylamide, N-[tris(hydroxymethyl)methyl]acrylamide, 4-hydroxybutyl acrylate, hydroxypropyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, hydroxypropyl methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, 1,4-butanediol vinyl ether, di(ethylene glycol)vinyl ether, ethylene glycol vinyl ether, N,N-1,2-dihydroxyethylene-bis-acrylamide, N,N-1,2-dihydroxyethylene-bis-methyacrylamide, N-hydroxymethyl methacrylamide, N-tri(hydroxymethyl)-methyl-methacrylamide, and any mixture of the foregoing.

[0097] Aspect 34. The coating composition of aspect 31, wherein the second polymer has a weight-average molecular weight (Mw) of between 50,000 and 800,000.

[0098] Aspect 35. The coating composition of aspect 24, additionally comprising water or a water/ alcohol mixture.

[0099] Aspect 36. A coated substrate comprising: a substrate and a lubricious coating made using a coating composition of any one of aspects 24-35.

[00100] Aspect 37. The coated substrate of aspect 36, additionally comprising a base coat that contacts both the substrate and the lubricious coating composition.

[00101] Aspect 38. The coated substrate of aspect 37, wherein the base coat is hydrophobic.

[00102] Aspect 39. The coated substrate of aspect 36, wherein the substrate is plastic.

[00103] Aspect 40. The coated substrate of aspect 36, wherein the substrate is metallic.

[00104] Aspect 41. The coated substrate of any one of aspects 36-40, wherein the coated substrate has a lubricity of less than 25 gf friction and a durability of less than 50 gf friction as measured by a pinch test.

[00105] Aspect 42. A medical device or medical implant comprising a coated substrate of any one of aspects 36-41.

[00106] Aspect 43. The medical device or medical implant of aspect 42 where the medical device or medical implant is sterilized by at least one of gamma-ray, E-beam, and ethylene oxide.

[00107] Aspect 44. The medical device or medical implant of aspect 42 or 43, where the lubricious coating contains a pharmaceutical or antimicrobial agent blended with the coating composition.

EXAMPLES

[00108] The invention is illustrated by the following non-limiting examples.

[00109] The following abbreviations are used herein:

MHB - 4-methacryloxy-2-hydroxybenzophenone was the monomer that provided photoactivity to the copolymer. It was purchased from Polysciences and Bimax. The purity was confirmed with nuclear magnetic resonance NMR done at USciences with a Bruker 400MHz NMR.

BA – butyl acrylate

MMA – methyl methacrylate

HEMA – hydroxyethyl methacrylate

NVP – N-vinyl pyrrolidone

EHMA – ethylhexyl methacrylate

iDMA – isodecyl methacrylate

DDMA – dodecyl methacrylate

AA – acrylic acid

HEAA – N-(2-hydroxyethyl)acrylamide

PVP – polyvinylpyrrolidone

HAP – hydrophilic acrylic copolymer, a copolymer of AA and HEAA

[00110] The coating was applied to a variety of substrates in the form of rods or tubing. The rods were stainless steel or PMMA with a diameter of 0.125 inches. Pebax™ 35D and 55D plastic tubing had an outer diameter of 0.079 inches and a wall thickness of 0.005 inches. The tubing was placed over stainless steel rod for stability before coating. The coating process consisted of wiping the rod with isopropyl alcohol, dip coating in basecoat solution at 0.2 in / sec, drying at 60 °C for 10 minutes, dip coating in topcoat solution at 0.2 in / sec, and drying at 60 °C for 10 minutes. Only after all coatings had been applied was the rod subjected to UV radiation.

[00111] UV cure was performed in an Uvitron IntelliRay model UV0832 UV Cure unit equipped with a UVA 600 Watt metal halide lamp. Irradiance was measured with an EIT Uvicure Plus II radiometer purchased from INPRO Technologies. This one channel UVA radiometer measures the radiation between 320 and 390 nanometers (nm).

[00112] Two different methods were used to provide uniform radiation around the rods. In the first method hexagonal couplers were attached to the rod to provide a fixed geometry for turning the coated rod as it was being cured. The sample could then be passed through 6 rotations to expose all sides. The rotation pattern was 0°, 120°, 240°, 60°, 180°, and 300°. In the second method the rod was rotated continuously by a motor at 20 rpm during UV cure.

[00113] Typical radiation times in the examples are 2-30 minutes and typical irradiance is 100-200 mW/cm2 (at 320-390 nm from a UVA metal halide lamp). It is noted that all of the 320-390 nm radiation is not useful in the photo-crosslinking, only the wavelengths that are actually absorbed by the photoactive group can lead to reaction. It is also understood that lower irradiance than that used in these examples can be accommodated by an increase in radiation time.

[00114] The friction of the coating was tested on a Chatillon CS225 Force Measurement Machine. It was equipped with a heated water bath and pinch pads that pressed together at a constant force. The water bath is filled PBS solution and heated to 37°C. The pinch pads are submerged in the water and pressed together with 470 grams (g) of force. The friction is measured as the grams of force required to push and pull the sample through the pads. The lubricity and durability are determined by averaging the grams of force when the samples are pulled through the pads. Lubricity is the average from cycle 1-3 and durability is the force during cycle 30.

[00115] Photoactive basecoats were made by copolymerizing 4-methacryloxy-2-hydroxybenzophenone and low glass temperature (meth) acrylate monomers. Photoactive basecoat polymers synthesized are summarized in table 1.

Table 1: Photoactive Basecoat Polymers

Basecoat Polymer	% MHB	Comonomer	Glass Temperature (degrees C, calculated)
BP-1	2	EHMA	25
BP-2	5	EHMA	29
BP-3	8	EHMA	33
BP-4	10	EHMA	33
BP-5	8	iDMA	17

BP-6	5	DDMA/MMA	6
BP-7	8	DDMA/MMA	7
BP-8	8	DDMA/BMA	10
BP-9	2	BA/MMA	7
BP-10	5	BA/MMA	8
BP-11	8	BA/MMA	9
BP-12	5	BA	-8
BP-13	0	BA/MMA	12

Basecoat Polymers also contain 12.7% HEMA and 21.7% NVP

[00116] Poly(methyl methacrylate) (PMMA) rods were coated with Basecoat Polymer BP-5 and polyvinylpyrrolidone (PVP) topcoat (Aldrich 1,300,000 molecular weight by light scattering). The coated rods were cured at an irradiance of 186 milliwats per square centimeter (mW/cm^2) through each of six rotations. After pinch testing, the rods were rinsed for 10 seconds under running cold tap water, immersed in 0.5% Congo Red aqueous solution, and then rinsed again for 10 seconds. The presence of bound PVP indicated by the intense red color demonstrated that grafting had occurred between the photoactive basecoat and the PVP topcoat.

[00117] PVP topcoat with four different UV cure basecoat polymers were tested over PMMA substrate rods. UV cure was done at an irradiance of 166 mW/cm^2 over 20 minutes at each of the six rotations. Although the samples exhibited fair lubricity, they only lasted 10-20 cycles. The results are summarized in table 2.

Table 2: UV Cure with PVP Topcoat and Different Basecoat Polymers

Basecoat Polymer	Basecoat Monomer	First cycle friction	Last cycle friction
BP-3	EHMA	53	66
BP-5	iDMA	38	62
BP-7	DDMA/MMA	77	94
BP-11	BA/MMA	72	95

A Hydrophilic Acrylic Polymer and blends of this Hydrophilic Acrylic Polymer with PVP were evaluated as topcoats (with added surfactant). The Hydrophilic Acrylic Polymer (HAP) was a copolymer of acrylic acid and 2-hydroxyethylacrylamide. The UV cure was six rotations at an irradiance of 180 mW/cm^2. The results are in table 3. All three rods of each sample exhibited good lubricity and durability through 30 cycles.

Table 3: Effect of Cure Time on Coating Performance of HAP/PVP Topcoat Blends

Topcoat	Cure time, minutes	Initial Friction	30th Cycle Friction	Bound Topcoat, micrograms/cm^2
HAP + PVP	6X30	17.3	16.5	44
HAP	6X30	21.3	11.6	71
HAP + PVP	6X15	6.32	4.8	38
HAP	6X15	6.17	4.8	63
HAP + PVP	6X5	9.02	4.8	7.8
HAP	6X5	9.876	19.9	11.8

Basecoat Polymer for all samples was BP-3 (EHMA) coated at 8% Solids.
Bound topcoat measures HAP portion of the bound topcoat

[00118] The results summarized in the above examples do indicate that good lubricity and durability can be obtained from a photoactive basecoat without any photoactivity in the topcoat. A disadvantage of the UV cure process used in these examples is that it requires stopping the UV cure and manually rotating the samples five times during the cure. To overcome this a motor was set up to continuously rotate the samples at 20 rpm during the cure. This is expected to provide even more uniform UV cure around the circumference of the rod or tubing. This method was not only more convenient, but as shown below provided even better lubricity and durability at even shorter cure times.

[00119] Table 4 shows a comparison of several compositions using different monomer compositions and different amounts of the photoactive monomer. Results indicate that a variety of low glass temperature monomers can be used to provide a lubricious, durable coating. These examples have no photoactive component in the topcoat.

Table 4: Effect of Amount of Photoactive Monomer and of Comonomer Composition

Basecoat Polymer	Basecoat Solids	Cure Time, minutes	Dynamic Friction, g, Cycles 1-3	Dynamic Friction, g, 30th Cycle	Bound Topcoat, micrograms/cm^2
BP-3	8%	2	24	> 340	0.8
BP-3	8%	6	18	270	1.3
BP-3	8%	20	12	59	9.6
BP-3	10%	20	14	17	39
BP-4	8%	20	10	15	39
BP-11	8%	20	12	17	36
BP-5	8%	20	9	17	36
BP-7	8%	20	10	17	36
BP-8	8%	20	12	15	37
BP-3	8%	20	22	22	19
BP-3	8%	6	21	24	12
BP-4	8%	6	16	40	11

BP-11	8%	6	16	17	10
BP-11	8%	2	18	260	4.5
BP-3	8%	2	16	320	3.3
BP-7	8%	2	15	260	2.8
BP-7	8%	6	12	240	5.2
BP-8	8%	2	16	290	1.7
BP-8	8%	6	16	290	2.1
BP-1	10%	20	14	46	29
BP-1	10%	6	18	180	25
BP-2	10%	20	15	20	26
BP-2	10%	6	13	55	12
BP-10	10%	20	14	18	24
BP-10	10%	6	14	34	8
BP-9	10%	20	14	38	19
BP-9	10%	6	16	67	4.3
BP-6	10%	20	18	29	8.2
BP-6	10%	6	17	43	1.4
BP-12	10%	6	17	18	5.7

Footnotes for Table 4:

Basecoat is coated over Pebax™ 55D tubing.

After drying basecoat, Poly(HEAA-co-AA) topcoat containing surfactant was added and dried before UV cure.

[00120] Coated rods with even better durability can be obtained by including some trifunctional aziridine such as trimethylolpropane tris(2-methyl-1-aziridine propionate) (Crosslinker CX-100) in the basecoat. Polyfunctional aziridines are known crosslinkers in thermal cure processes. The results in table 5 demonstrate the increase in durability.

Table 5: Effect of Trifunctional Aziridine

Polymer	Basecoat Solids	Trifunctional aziridine	Cure Time, minutes	Dynamic Friction, g, Cycles 1-3	Dynamic Friction, g, 30th Cycle	Bound Topcoat, micrograms/cm^2
BP-2	10%	0	20	17	28	3.5
BP-2	10%	0	6	18	64	2.0
BP-2	10%	0.087%	20	17	16	39
BP-2	10%	0.087%	6	23	30	52
BP-10	10%	0.0425%	6	22	29	69
BP-10	10%	0.0425%	6 (+ heat)	20	21	67
BP-10	10%	0.0843%	6	26	26	66
BP-10	10%	0.0843%	6 (+ heat)	26	24	66
BP-2	10%	0.0845%	6	17	124	58
BP-2	10%	0.0845%	6*	11	180	40
BP-10	10%	0.0845%	6	16	15	59
BP-10	10%	0.0845%	6*	14	23	59
BP-6	10%	0.0845%	6	12	370	56
BP-6	10%	0.0845%	6*	15	280	28
BP-12	10%	0.0845%	6	19	16	68

BP-12	10%	0.0845%	6*	19	19	63
BP-13	10%	0.082%	6	25	240	69
50% BP-13 / 50% BP-4	10%	0.082%	6	23	27	58
BP-4	10%	0.082%	6	15	14	49

Footnotes for Table 5:

Basecoat is coated over Pebax™ 55D tubing.

After drying basecoat, a poly(HEAA-co-AA) topcoat was added and dried.

6 (+ heat) indicates that the samples were heated at 60 °C for 30 minutes after UV cure.

6* indicates that the samples were soaked in aqueous PBS solution for 18 hours at 50 °C before pinch testing.

[00121] The aforementioned examples demonstrate that the combination of the photoactive basecoats of this invention and a hydrophilic topcoat with no inherent photoactivity provides good lubricity and durability. The following examples illustrate that even better performance can be obtained if photoactivity is also engineered into the topcoat.

[00122] Poly(HEAA-co-AA) in Table 6. The polymer was made by reacting 29.79 g of N-(2-hydroxyethyl)acrylamide (HEAA), 6.21 g of acrylic acid (AA) in 263 mL of water. The initiator for the polymerization was ammonium persulfate and sodium hydroxymethansulfinate hydrate. 0.015 mL of a 1% solution of $FeSO_4$ was added to catalyze the reaction. The polymerization was done under N_2 at 40°C. The polymer was purified by dialysis or precipitation with acetone (similar to Example 1 of US2013/0323291 A1).

[00123] Poly(HEAA-co-AA-co-MHB) 1-4 in Table 6. The photo-active polymer was made by reacting 15.29 g of HEAA, 3.19 g of AA and 1.00 g, 0.50 g, or 0.25 g of MHB in 40 mL of IPA and 30mL of water. 0.59 mL of a 50 mg/mL solution of Azobisisobutyronitrile (AiBN) in THF was added to the monomer solution. The solution was sparged for 30 minutes to remove the oxygen, then heated to 60 °C for 24 hours. After the reaction was complete the polymer was precipitate with 150 mL of ethyl acetate. The solvent was decanted off and the polymer then dried in an oven at 60 °C with any remaining solvent being removed under vacuum. The polymer was dissolved in a 50:50 mixture of IPA and water.

[00124] Poly(HEAA-co-AA-co-MHB) 5-7 in Table 6. The photo-active polymer was made by reacting 15.29 g of HEAA, 3.19 g of AA and 1.00 g, 0.50 g or 0.25 g of MHB in 40 mL of ethanol and 30mL of water. 0.245 mL of a 20 mg/mL solution of (AiBN) in THF

was added to the monomer solution. The solution was sparged for 30 minutes to remove the oxygen then heated to 60 °C for 24 hours. After the reaction was complete the polymer was precipitate with 150 mL of ethyl acetate. The solvent was decanted off and the polymer then dried in an oven at 60 °C with any remaining solvent removed under vacuum. The polymers were dissolved in a 50:50 mixture of ethanol and water.

[00125] The molecular weights of these hydrophilic photoactive polymers were determined through SEC using a Waters 1515 isocratic high performance liquid chromatography HPLC pump, Waters 2489 UV/Visible detector set to 276 nm and 290 nm, Waters 2414 Refractive Index Detector, and 3 columns (2 Waters Ultrahydrogel 2000 and 1 Waters Ultrahydrogel 250). The molecular weights were calculated by comparing to poly (acrylic acid) standards using Empower 3 software.

Table 6: Composition and M_w and M_n for the Photoactive Hydrophilic Polymers

Poly(HEAA-co-AA-co-MHB)	Mole% MHB	M_w	M_n	M_w/ M_n
1	2	72,417	19,150	3.78
2	1	58,864	12,757	4.61
3	1	191,290	55,687	3.44
4	0.5	216,586	74,642	2.94
5	2	218,178	79,888	2.73
6	1	254,733	69,063	3.69
7	0.5	231,294	75,766	3.05
Poly(HEAA-co-AA)	0	649,456	301,998	2.15

[00126] The coating was applied to a Pebax™ 55D plastic tubing using the dip-coating method. The Pebax™ tubing had an outer diameter of 0.201 cm (0.079 inches) and a wall thickness of 0.0127 cm (0.005 inches). The tubing was placed over stainless steel rod for stability. The tubing was first dipped into the basecoat and extracted at 0.508 cm (0.2 inches) per second and was rotated in UV chamber for 5 minutes set to the desired intensity. Then the tubing was dipped into the topcoat and extracted at 0.508 cm (0.2 inches) per second and was rotated in UV chamber for 5 minutes set to the desired intensity.

[00127] UV cure was performed in an Uvitron IntelliRay model UV0832 UV Cure unit equipped with a UVA 600 Watt metal halide lamp. Irradiance was measured with an EIT Uvicure Plus II radiometer purchased from INPRO Technologies. This one channel UVA radiometer measures the radiation between 320 and 390 nm.

[00128] The friction of the coating was pinch tested on a Tinius Olsen 5ST Electromechanical Testing Machine with a 10N load cell and the data was collected with

Horizon software. The Tinius Olsen is equipped with a heated water bath and pinch pads that pressed together at a constant force. The water bath is filled with PBS solution and heated to 37°C. The pinch pads are submerged in the water and pressed together with 450 g of force. The friction is measured as the grams of force required to push and pull the sample through the pads. The lubricity and durability are determined by averaging the grams of force when the samples are pulled through the pads. Lubricity is the average from cycle 2-4 and durability is the average from cycle 28-30.

[00129] Basecoat solutions were made using two of the photo-active basecoat polymers described previously. The Basecoat polymer can be diluted with a variety of different solvents including Isopropanol (IPA) and Ethanol. Basecoat A: 10 wt% solution of a copolymer of 2-ethylhexyl methacrylate (EHMA), N-vinylpyrrolidone (NVP), (hydroxyethyl)methacrylate (HEMA), and MHB in propylene glycol methyl ether acetate, PMA, with a polyaziridine crosslinker. Basecoat B: 10 wt% solution of a copolymer of butyl acrylate (BA), methyl methacrylate (MMA), NVP, HEMA, and MHB in PMA with a polyaziridine crosslinker.

[00130] Pebax™ 55D tubing was coated with Basecoat A and, after the 5 minute uv cure, this was coated with the topcoats containing the photoactive polymers described in table 6, along with 2% Poly(HEAA-co-AA) and surfactants in water. Table 7 shows the results of the friction test of the different topcoats curing with different UV light intensities.

Table 7: Testing of Different Photoactive Topcoats over Basecoat A

	Basecoat	Poly(HEAA-co-AA-co-MHB) (Wt%)	Poly(HEAA-co-AA) (Wt%)	Intensity (mW/cm^2)	Lubricity (gf)	Durability (gf)	Pads
1	A	1% (19kMn/2% MHB)	2%	130	14±0.8	14±1.0	Silicone
2	A	1% (19kMn/2% MHB)	2%	90	10±0.9	13±0.2	Silicone
3	A	1% (19kMn/2% MHB)	2%	90	12±0.2	17±6.1	Delrin
4	A	0.5% (19kMn/2% MHB)	2%	90	12±0.6	14±2.6	Delrin
5	A	1% (13kMn/1% MHB)	2%	90	12±4.0	25±13	Delrin
6	A	1% (56kMn/1% MHB)	2%	90	19±3.7	45±20	Delrin
7	A	0.5% (56kMn/1% MHB)	2%	90	15±1.6	41±3.1	Delrin

8	A	1% (75kMn/0.5% MHB)	2%	90	18±8.3	116±105	Delrin
9	A	1% (69kMn/1% MHB)	2%	90	14±1.2	16±6.4	Delrin
10	A	0.5% (69kMn/1% MHB)	2%	90	16±2.8	44±32	Delrin
11	A	1% (69kMn/1% MHB)	2%	130	12±0.8	26±7.6	Delrin
12	A	0.5% (69kMn/1% MHB)	2%	130	14±2.3	31±11	Delrin
13	A	1% (80kMn/2% MHB)	2%	90	11±1.6	85±9.2	Delrin
14	A	0.5% (80kMn/2% MHB)	2%	90	13±4.0	111±25	Delrin
15	A	1% (80kMn/2% MHB)	2%	130	16±5.4	105±34	Delrin
16	A	0.5% (80kMn/2% MHB)	2%	130	13±5.8	75±33	Delrin
17	A	1% (76kMn/0.5% MHB)	2%	90	13±4.0	144±69	Delrin
18	A	1% (76kMn/0.5% MHB)	2%	130	12±2.2	16±10	Delrin

[00131] Table 8 shows the results of the friction test of the different topcoats using Basecoat B. The photo-active topcoat contained a Poly(HEAA-co-AA-co-MHB) described in table 1, Poly(HEAA-co-AA), and surfactants in water.

Table 8: Testing of Different Photoactive Topcoats over Basecoat B

	Basecoat	Poly(HEAA-co-AA-co-MHB) (Wt%)	Poly(HEAA-co-AA) (Wt%)	IPA (Wt%)	Intensity (mW/cm^2)	Lubricity (gf)	Durability (gf)	Pads
1	B	1% (19kMn/2% MHB)	2%	none	90	36±9.8	50±26	Delrin
2	B	1% (19kMn/2% MHB)	2%	10	90	9.6±1.4	10±0.2	Delrin
3	B	0.5% (19kMn/2% MHB)	2%	none	90	38±2.3	83±67	Delrin
4	B	0.5% (19kMn/2% MHB)	2%	10	90	14±1.3	15±1.3	Delrin
5	B	1% (80kMn/2% MHB)	2%	10	90	16±5.9	20±12	Delrin

[00132] The examples of table 9 illustrate that the photoactive basecoats perform well when directly applied to the substrate. That is, a hydrophobic basecoat is not necessary for good lubricity and durability with the photoactive hydrophilic topcoat. The photoactive

topcoats were applied twice with a 5 minute cure after each application. As above the topcoat solutions comprised one of the photoactive topcoats of table 6, Poly(HEAA-co-AA), and surfactants in water.

Table 9: Direct Application of Hydrophilic Topcoat onto Pebax™ 55D Substrate

	Poly(HEAA-co-AA-co-MHB) (Wt%)	Poly(HEAA-co-AA) Wt%	Intensity (mW/cm^2)	Lubricity (gf)	Durability (gf)	Pads
1	1% (19kMn/2% MHB)	2%	130	12±1.4	15±1.8	Silicone
2	1% (19kMn/2% MHB)	2%	90	9±2.3	100±74	Silicone
3	1% (19kMn/2% MHB)	2%	130	52±6.8	158±3.7	Delrin
4	1% (19kMn/2% MHB)	2%	90	51±6.4	132±14	Delrin
5	1% (69kMn/1% MHB)	2%	130	6±4.5	76±57	Silicone
6	1% (69kMn/1% MHB)	2%	90	5±1.1	29±36	Silicone
7	1% (69kMn/1% MHB)	2%	130	29±8.3	104±20	Delrin
8	1% (69kMn/1% MHB)	2%	90	51±6.6	108±3.2	Delrin

[00133] Throughout this specification, words are to be afforded their normal meaning, as would be understood by those skilled in the relevant art, unless otherwise indicated. However, so as to avoid misunderstanding, the meanings of certain terms will be specifically defined or clarified.

[00134] In the present disclosure the singular forms "a," "an," and "the" include the plural reference, and reference to a particular numerical value includes at least that particular value, unless the context clearly indicates otherwise. Thus, for example, a reference to "a material" is a reference to at least one of such materials and equivalents thereof known to those skilled in the art, and so forth.

[00135] It is to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. As used in the specification and in the claims, the term "comprising" can include the embodiments "consisting of" and "consisting essentially of." Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. In this specification and in the

claims which follow, reference will be made to a number of terms which shall be defined herein.

[00136] When a value is expressed as an approximation by use of the descriptor "about," it will be understood that the particular value forms another embodiment. In general, use of the term "about" indicates approximations that can vary depending on the desired properties sought to be obtained by the disclosed subject matter and is to be interpreted in the specific context in which it is used, based on its function. The person skilled in the art will be able to interpret this as a matter of routine. In some cases, the number of significant figures used for a particular value may be one non-limiting method of determining the extent of the word "about." In other cases, the gradations used in a series of values may be used to determine the intended range available to the term "about" for each value.

[00137] Where present, all ranges are inclusive and combinable. That is, references to values stated in ranges include every value within that range including the endpoint values.

[00138] When a list is presented, unless stated otherwise, it is to be understood that each individual element of that list and every combination of that list is to be interpreted as a separate embodiment. For example, a list of embodiments presented as "A, B, or C" is to be interpreted as including the embodiments, "A," "B," "C," "A and B," "A and C," "B and C," or "A, B, and C."

[00139] It is to be appreciated that certain features of the invention which are, for clarity, described herein in the context of separate embodiments, may also be provided in combination in a single embodiment. That is, unless obviously incompatible or specifically excluded, each individual embodiment is deemed to be combinable with any other possible embodiment(s) and such a combination is considered to be another embodiment. Conversely, various features of the invention that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. Further, while an embodiment may be described as part of a series of steps or part of a more general structure, each said step or part may also be considered an independent embodiment in itself.

[00140] As used herein, the terms "article" and "substrate" are not limited to any shape or size, as it may be a layer of material, multiple layers or a block having at least one surface of which is modified by a coating composition described herein.

[00141] Glass transition temperature (Tg) is determined using the *Fox* equation and literature values of the homopolymers. The Fox equation is as follows:

$$1 / T_{g,mix} \approx \sum_i \omega_i / T_{g,i}$$

where $T_{g,mix}$ and $T_{g,i}$ are the glass transition temperatures in degrees Kelvin of the mixture / copolymer and of the components, respectively, and ω_i is the mass fraction of component *i*. Monomers that produce low T_g homopolymers are required to produce copolymers with low T_g's. Examples include butyl acrylate (Tg = -54 degrees C), 2-ethylhexyl methacrylate (-10), isodecyl methacrylate (-30), and dodecyl methacrylate (-65). The homopolymer Tg's of some of the other monomers used are 100 °C for MMA, 20 °C for BMA, 120 °C for NVP, 105 °C for HEMA, 143 °C for MHB and 105 °C for acrylic acid.

[00142] For two components A and B, the Fox equation reduces to

$$1 / T_{g,mix} \approx \omega_A / T_{g,A} + \omega_B / T_{g,B}$$

[00143] As used herein the term "hydrophobic" refers to a polymer that is not soluble in aqueous solutions. A crosslinked hydrophobic polymer does not swell significantly in water (less than 50%, <50%).

[00144] The term "hydrophilic" refers to a polymer that is soluble in water or water-alcohol solutions. A crosslinked hydrophilic polymer swells significantly in aqueous solutions (>100%). A "hydrophilic" substrate surface is one made of a polymer where the uncured or non-crosslinked polymer is soluble in water or in a water alcohol solution that is more than 50% water.

[00145] Unless otherwise specified, all molecular weights are weight-average molecular weights (Mw).

What is claimed:

1. A coating composition comprising hydrophobic polymer for use as a photoreactive basecoat for a medical device or implant comprising a polymer made from monomers comprising:

(a) 1 to 12 mol % of at least one photoactive monomer that is a hydrogen atom abstracter, and

(b) 99 to 88 mol % of one or more of acrylamides, methacrylamides, acrylates, methacrylates, and N-vinylpyrrolidone;

wherein the polymer has a glass transition temperature (Tg) of less than 40 °C.

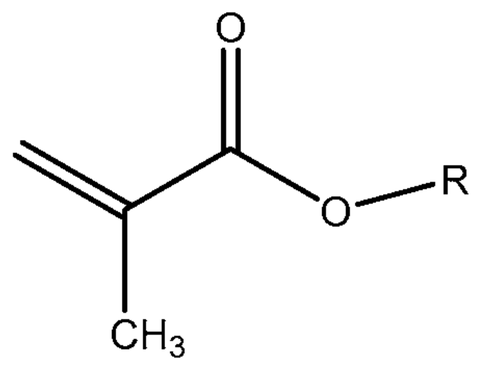
2. The coating composition of claim 1, additionally comprising a multifunctional aziridine.

3. The coating composition of claim 2, comprising

(a) 95-99.8 wt % of the hydrophobic polymer; and

(b) 0.2-5 wt % multifunctional aziridine.

4. The coating composition of anyone of claims 1-3, comprising methacrylate of the structure



where R is an optionally substituted C_1-C_{20} alkyl.

5. The coating composition of claim 4, wherein R is one or more of methyl, ethylhexyl, isodecyl, or dodecyl.

6. The coating composition of claim 4, wherein the hydrophobic polymer comprises hydroxyethyl methacrylate and N-vinylpyrrolidone.

7. The coating composition of anyone of claims 1-6, wherein the hydrophobic polymer comprises acrylate having a C_4-C_{20} alkyl group.

8. The coating composition of anyone of claims 1-7, wherein the photoactive monomer that is a hydrogen atom abstracter comprises a benzophenone moiety.

9. The coating composition of claim 8, wherein the photoactive monomer that is a hydrogen atom abstracter comprises one or more of 4-methacryloxy-2-hydroxybenzophenone, 4-acryloxybenzophenone, 4-methacryloxybenzophenone, acrylamidobenzophenone, methacrylamidobenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone, and 2-hydroxy-4-methacryloxyethoxybenzophenone.

10. The coating composition of anyone of claims 1-9 having a Tg of less than 20 °C.

11. A medical device or implant comprising a photoreactive basecoat comprising a coating composition of any one of claims 1-10.

12. The medical device of claim 11, wherein the basecoat resides between a substrate and a hydrophilic topcoat.

13. The medical device of claim 12, wherein the topcoat comprises one or more of polyacrylate, polyvinylpyrrolidones, hyaluronic acid and polyacrylamide.

14. The medical device of claim 12, wherein the topcoat comprises a N-(2-hydroxyethyl)acrylamide and acrylic acid copolymer.

15. The medical device of claim 11, wherein the medical device is a catheter or guide wire.

16. The medical device of claim 12, comprising a plurality of covalent cross-links between said basecoat and said hydrophilic topcoat.

17. A coating solution comprising 2 to 15 wt% of a coating composition of any one of claims 1-10 in a solvent.

18. The coating solution of claim17, wherein the solvent is an organic solvent.

19. The coating solution of claim 18, wherein the solvent comprises one or more of toluene, ethanol, acetone, isopropanol, ethyl acetate, dimethylformamide, tetrahydrofuran, butanol, N-methyl-2-pyrrolidon, n-butyl acetate, 1,2-propanediol monomethyl ether acetate, isobutyl acetate, isopropyl acetate, methyl acetate, 3-methyl-1-butanol, methylethyl ketone, 2-methyl-1-propanol, 1-pentanol, 2-propanol, propyl acetate, dichloromethane, dimethyl sulfoxide, methylbutyl ketone and xylene.

20. A method of forming a coated article comprising coating a substrate with a basecoat comprising a coating composition of any one of claims 1-10.

21. The method of claim 20, additionally comprising curing the basecoat by exposure of the basecoat to UV light.

22. The method of claim 21, additionally comprising coating said basecoat with a hydrophilic topcoat.

23. The method of claim 20, additionally comprising (a) coating said basecoat with a hydrophilic topcoat and (b) curing the basecoat and topcoat with UV light.

24. A coating composition for medical devices or medical implants comprising a polymer which is soluble in water or water-alcohol solutions, the polymer made from monomers comprising:

(a) at least one monomer that is a photo radical generator comprising one or more of 4-methacryloxy-2-hydroxybenzophenone, 4-acryloxybenzophenone, 4-methacryloxybenzophenone, acrylamidobenzophenone, methacrylamidobenzophenone, 2-hydroxy-4-acryloxyethoxybenzophenone, 2,4-dihydroxy-4'-vinyl benzophenone, and 2-hydroxy-4-methacryloxyethoxybenzophenone, and

(b) at least one monomer comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides;

wherein the ethylenic monomers comprise at least one acidic group comprises acrylic acid, methacrylic acid, 2-ethylacrylic acid, 2-propylacrylic acid, acryloxypropionic acid,

isocrotonic acid, maleic anhydride, maleic acid and half esters, half amides and half thioesters of maleic acid, fumaric acid and itaconic acid, and mixtures thereof;

wherein the acrylates or acrylamides comprise acrylamide, N-(2-hydroxyethyl)acrylamide, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, and N-(2-hydroxyethyl) methacrylamide, N-acryloylamido-ethoxyethanol, N-(hydroxymethyl) acrylamide, N-[tris(hydroxymethyl)methyl]acrylamide, 4-hydroxybutyl acrylate, hydroxypropyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, hydroxypropyl methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, 1,4-butanediol vinyl ether, di(ethylene glycol)vinyl ether, ethylene glycol vinyl ether, N,N-1,2-dihydroxyethylene-bis-acrylamide, N,N-1,2-dihydroxyethylene-bis-methyacrylamide, N-hydroxymethyl methacrylamide, N-tri(hydroxymethyl)-methyl-methacrylamide, or any mixture of the foregoing;

wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator group is 20:1 to 500:1.

25. The coating composition of claim 24, wherein the photo radical generator group comprises 4-methacryloxy-2-hydroxybenzophenone.

26. The coating composition of claim 24, wherein the ethylenic monomers comprise N-(2-hydroxyethyl)acrylamide and acrylic acid.

27. The coating composition of claim 26, wherein the molar ratio of N-(2-hydroxyethyl)acrylamide to acrylic acid is 2:1 to 5:1.

28. The coating composition of claim 24, wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator comprising at least one photopolymerizable group is 40:1 to 200:1.

29. The coating composition of claim 24, wherein the polymer has a weight-average molecular weight (Mw) of between 20,000 and 800,000.

30. The coating composition of claim 24, additionally comprising a second polymer which is soluble in water or water-alcohol solutions.

31. The coating composition of claim 30, comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides.

32. The coating composition of claim 31, wherein the ethylenic monomers of the second polymer comprise at least one acidic group, the ethylenic monomers of the second polymer comprising the at least one acidic group comprise one or more of acrylic acid, methacrylic acid, 2-ethylacrylic acid, 2-propylacrylic acid, acryloxypropionic acid, isocrotonic acid, maleic anhydride, maleic acid and half esters, half amides and half thioesters of maleic acid, fumaric acid, itaconic acid, and any combination thereof.

33. The coating composition of claim 31, wherein the acrylates or acrylamides of the second polymer comprise acrylamide, N-(2-hydroxyethyl)acrylamide, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, , and N-(2-hydroxyethyl) methacrylamide, N-acryloylamido-ethoxyethanol, N-(hydroxymethyl) acrylamide, N-[tris(hydroxymethyl)methyl]acrylamide, 4-hydroxybutyl acrylate, hydroxypropyl acrylate, methyl 3-hydroxy-2-methylenebutyrate, hydroxypropyl methacrylate, 2-allyloxyethanol, 3-allyloxy-1,2-propanediol, 1,4-butanediol vinyl ether, di(ethylene glycol)vinyl ether, ethylene glycol vinyl ether, N,N-1,2-dihydroxyethylene-bis-acrylamide, N,N-1,2-dihydroxyethylene-bis-methyacrylamide, N-hydroxymethyl methacrylamide, N-tri(hydroxymethyl)-methyl-methacrylamide, and any mixture of the foregoing.

34. The coating composition of claim 31, wherein the second polymer has a weight-average molecular weight (Mw) of between 50,000 and 800,000.

35. The coating composition of claim 24, additionally comprising water or a water/ alcohol mixture.

36. A coated substrate comprising:

-- a substrate and

-- a lubricious coating made using a coating composition of any one of claims 24-35.

37. The coated substrate of claim 36, additionally comprising a base coat that contacts both the substrate and the lubricious coating composition.

38. The coated substrate of claim 37, wherein the base coat is hydrophobic.

39. The coated substrate of claim 36, wherein the substrate is plastic.

40. The coated substrate of claim 36, wherein the substrate is metallic.

41. The coated substrate of any one of claims 36-40, wherein the coated substrate has a lubricity of less than 25 gf friction and a durability of less than 50 gf friction as measured by a pinch test.

42. A medical device or medical implant comprising a coated substrate of any one of claims 36-41.

43. The medical device or medical implant of claim 42 where the medical device or medical implant is sterilized by at least one of gamma-ray, E-beam, and ethylene oxide.

44. The medical device or medical implant of claim 42 or 43, where the lubricious coating contains a pharmaceutical or antimicrobial agent blended with the coating composition.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/56578

A. CLASSIFICATION OF SUBJECT MATTER
IPC - A61L 29/08; A61L 29/14 (2021.01)
CPC - A61L 29/085; A61L 29/14;A61L 29/085, C08L3 3/08

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)
See Search History document

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2007/0032882 A1 (Lodhi et al.) 08 February 2007 (08.02.2007); Abstract para[0010] para[0012] para[0016] para[0053] para[0069] para[0070] para[0071] para[0077]	1, 4-6 --------- 2-3
X	US 2011/0134387 A1 (Samuel et al.) 09 June 2011 (09.06.2011); Abstract para[0010] para[0052] para[0057] para[0068] para[0091] para[0095] para[0135]	24-40
Y	US 2007/0286959 A1 (Palmer) 13 December 2007 (13.12.2007); para[0010]	2-3
A	US 2007/0141365 A1 (Jelle et al.) 21 June 2007 (21.06.2007); entire document	1-6, 24-40
A	US 2017/0281831 A1 (Surmodics, Inc) 05 October 2017 (05.10.2017); entire document	1-6, 24-40
A	US 2012/0178872 A1 (Blanquer et al.) 12 July 2012 (12.07.2012); entire document	1-6, 24-40
A	US 2011/0063567 A1 (Domschke et al.) 17 March 2011 (17.03.2011); entire document	1-6, 24-40
A	US 2002/0037984 A1 (Vanderbilt) 28 March 2002 (28.03.2002); entire document	1-6, 24-40

☐ 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
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
08 February 2021 (08.02.2021)	MAR 30 2021
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 20/56578

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:

3. ☒ Claims Nos.: 7-23, 41-44
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:

--------See Supplemental Box----------

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

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

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

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US 20/56578

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-6 drawn to a coating composition comprising hydrophobic polymer for use as a photoreactive basecoat for a medical device or implant comprising a polymer made from monomers comprising: (a) 1 to 12 mol % of at least one photoactive monomer that is a hydrogen atom abstracter, and (b) 99 to 88 mol % of one or more of acrylamides, methacrylamides, acrylates, methacrylates, and N-vinylpyrrolidone; wherein the polymer has a glass transition temperature (Tg) of less than 40 oC

Group II: Claims 24-40 drawn to a coating composition for medical devices or medical implants comprising a polymer which is soluble in water or water-alcohol solutions, the polymer made from monomers comprising: (a) at least one monomer that is a photo radical generator; (b) at least one monomer comprising one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides; wherein the molar ratio of one or both of (i) ethylenic monomers comprising at least one acidic group and (ii) one or more of acrylates or acrylamides to photo radical generator group is 20:1 to 500:1

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group I requires a coating composition comprising hydrophobic polymer, wherein the polymer has a glass transition temperature (Tg) of less than 40 oC, not required by Group II

Group II requires a coating composition comprising a polymer which is soluble in water or water-alcohol solutions, not required by Group I

Shared Common Features

Groups I-II share technical feature of a coating composition comprising a polymer for medical devices or medical implants, the polymer made from monomers comprising: (a) at least one photoactive monomer; and (b) at least one monomer comprising one or more of acrylates or acrylamides. However, theses shared technical feature does not represent a contribution over prior art, because the shared technical feature as being anticipated by US 2017/0281831 A1 to Surmodics, Inc (hereinafter 'Surmodics'). Surmodics discloses a coating composition (Abstract "Embodiments of the disclosure include lubricious coatings") comprising a polymer for medical devices (Abstract "In an embodiment the disclosure includes a lubricious coating for a medical device"), the polymer made from monomers comprising: (a) at least one photoactive monomer; and (b) at least one monomer comprising acrylamide (Abstract "In an embodiment the disclosure includes a lubricious coating for a medical device including an acrylic acid polymer, an acrylamide copolymer comprising at least one photoreactive group, and a cross-linking agent comprising at least two photoreactive groups").

As the technical features were known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups. Groups I-II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.

Note Re: Item 4: claims 7-23, and 41-44 are determined unsearchable because they are not drafted in accordance with the second and third sentences of Rule 6.4(a).