



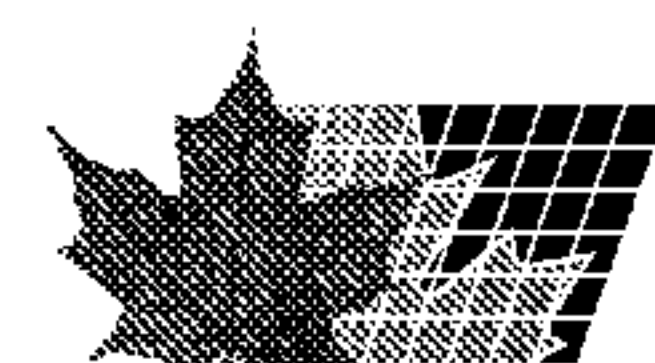
(86) **Date de dépôt PCT/PCT Filing Date:** 2014/02/14
(87) **Date publication PCT/PCT Publication Date:** 2014/08/21
(85) **Entrée phase nationale/National Entry:** 2015/08/11
(86) **N° demande PCT/PCT Application No.:** US 2014/016621
(87) **N° publication PCT/PCT Publication No.:** 2014/127304
(30) **Priorités/Priorities:** 2013/02/15 (US61/765,679);
2013/09/06 (US61/874,941); 2013/09/10 (US61/876,195)

(51) **Cl.Int./Int.Cl.** *B05D 5/08* (2006.01),
B05D 1/00 (2006.01), *B05D 3/02* (2006.01),
F28F 13/18 (2006.01)
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(54) **Titre : SURFACES POLYMERES GREFFEES POUR CONDENSATION GOUTTE A GOUTTE, ET PROCEDES ASSOCIES
D'UTILISATION ET DE FABRICATION**
(54) **Title: GRAFTED POLYMER SURFACES FOR DROPWISE CONDENSATION, AND ASSOCIATED METHODS OF USE AND
MANUFACTURE**

(57) **Abrégé/Abstract:**

Presented herein are articles and methods featuring substrates with thin, uniform polymeric films grafted (e.g., covalently bonded) thereupon. The resulting coating provides significant reductions in thermal resistance, drop shedding size, and degradation rate during dropwise condensation of steam compared to existing coatings. Surfaces that promote dropwise shedding of low-surface tension condensates, such as liquid hydrocarbons, are also demonstrated herein.



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

(19) World Intellectual Property
Organization
International Bureau



WIPO | PCT



(10) International Publication Number

WO 2014/127304 A1

(43) International Publication Date
21 August 2014 (21.08.2014)

(51) International Patent Classification:

B05D 5/08 (2006.01) *F28F 13/18* (2006.01)
B05D 1/00 (2006.01) *B05D 3/02* (2006.01)

(21) International Application Number:

PCT/US2014/016621

(22) International Filing Date:

14 February 2014 (14.02.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/765,679	15 February 2013 (15.02.2013)	US
61/874,941	6 September 2013 (06.09.2013)	US
61/876,195	10 September 2013 (10.09.2013)	US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

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

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

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) Title: GRAFTED POLYMER SURFACES FOR DROPWISE CONDENSATION, AND ASSOCIATED METHODS OF USE AND MANUFACTURE

(57) Abstract: Presented herein are articles and methods featuring substrates with thin, uniform polymeric films grafted (e.g., covalently bonded) thereupon. The resulting coating provides significant reductions in thermal resistance, drop shedding size, and degradation rate during dropwise condensation of steam compared to existing coatings. Surfaces that promote dropwise shedding of low-surface tension condensates, such as liquid hydrocarbons, are also demonstrated herein.



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GRAFTED POLYMER SURFACES FOR DROPWISE CONDENSATION, AND ASSOCIATED METHODS OF USE AND MANUFACTURE

Field of the Invention

[0001] This invention relates generally to grafted polymer surfaces and their use for enhanced heat transfer, improved dropwise condensation, and/or reduced adhesion of liquids and solids thereto.

Related Applications

[0002] This application claims priority to and the benefit of U.S. Provisional Patent Application No. 61/876,195, filed September 10, 2013, U.S. Provisional Patent Application No. 61/874,941, filed September 6, 2013, and U.S. Provisional Patent Application No. 61/765,679, filed February 15, 2013, the contents of which are hereby incorporated by reference herein in their entireties.

Government Support

[0003] This invention was made with government funding support from the NSF GRFP and support from NSF Career award no. ECS-0335765. This research was performed in part at the Institute for Soldier Nanotechnologies (ISN) supported in part by the U.S. Army Research Office under contract W911NF-13-D-0001. The United States Government has certain rights in this invention.

Background of the Invention

[0004] Vapors condense upon a surface if the surface is cooled below the saturation temperature at a given pressure. The condensed liquid phase may accumulate on the surface as a film and/or as droplets or islands of liquid. Condensation is critical in many industrial applications, although in certain applications, it is useful to inhibit or prevent the filmwise buildup of condensing liquid on a surface by promoting droplet shedding and enhancing dropwise condensation.

[0005] Condensation of water is a crucial process in many industries, including power generation and desalination. Roughly 85% of the global installed base of electricity generation plants and 50% of desalination plants worldwide rely on steam surface condensers, a type of heat exchanger in which a plurality of tubes flowing coolant contact steam on their outside surface. Given the widespread scale of these processes, even slight improvements in cycle efficiencies will have a significant effect on global energy consumption.

[0006] One useful measure of heat transfer performance for a condenser is the heat transfer coefficient, defined as the flux per area in units of $\text{kW/m}^2\text{K}$. Heat transfer coefficients experienced when condensing in the dropwise mode are an order of magnitude greater than those in the filmwise mode. The presence of an insulating liquid film during filmwise condensation presents a significant thermal barrier to heat transfer, whereas the departure of discrete drops during dropwise condensation exposes the condensing surface to vapor. The higher heat transfer coefficients experienced during dropwise condensation make it attractive for employing in large-scale thermal fluids applications such as steam power plants and desalination plants, as well as small-area

high-heat flux applications such as electronics cooling. However, the practical implementation of dropwise condensation in power generation, desalination, and other applications has been a significant materials challenge, limited by, among other factors, durability of existing hydrophobic functionalization for metal heat transfer surfaces. While metals provide both high thermal conductivity for maximizing heat transfer and high tensile strength to minimize the need for structural supports, metals are typically wetted by water and most other thermal fluids, and, as a result, metals exhibit filmwise condensation. In order for a metal surface to exhibit desired dropwise condensation, the surface that is used for heat transfer needs to be modified. One way to achieve dropwise condensation on a metal surface where heat transfer takes place is to modify the metal surface with a hydrophobic coating.

[0007] A number of conventional techniques have been employed previously to promote dropwise condensation on surfaces, including the use of monolayer promoters such as oleic acid and stearic acid (U.S. Patent No. 2,919,115), noble metals (U.S. Patent No. 3,289,753 and U.S. Patent No. 3,289,754 and U.S. 3,305,007), ion-implanted metal (U.S. Patent No. 6,428,863), as well as thin films of polymers applied via sputtering or dip-coating (U.S. Patent No. 2,923,640, U.S. Patent No. 3,899,366, EP2143818 A1, U.S. Patent No. 3,466,189). However, previous methods suffer from problems such as low durability and/or high cost. Moreover, most of these hydrophobic modifiers, and especially the silane-based modifiers that have been used in some conventional methods, are not robust in steam environments of industrial interest (in other words, these modifiers cannot withstand the environments in which they are used). Previous methods also do not adequately promote rapid droplet shedding because they do not sufficiently

reduce the contact angle hysteresis. It is possible to have a surface with a high contact angle but also high adhesion, so even though condensation would initiate in the dropwise regime, it would ultimately progress to filmwise condensation because the drops are not able to shed easily.

[0008] Furthermore, where the condensing liquids are hydrocarbons or other low-surface tension liquids, the problem of film-wise condensation is exacerbated. Current surfaces designed for dropwise condensation of water do not promote dropwise condensation of low-surface tension hydrocarbon liquids such as *n*-alkanes (e.g., octane, hexane, heptane, pentane, butane) and refrigerants (e.g., fluorocarbons, chlorofluorocarbons, hydrochlorofluorocarbons) and cryogenic liquids (e.g., LNG, O₂, N₂, CO₂, methane, propane).

[0009] Some conventional methods have used nanotextured surface to improve condensation heat transfer, however, these methods also rely on silane or thiol modifiers to modify the wettability of a nanotextured surface from superhydrophilic to superhydrophobic, and thus these nanotextured surfaces are subject to the same robustness concerns discussed above. Additionally, because the thermal conductivities of polymeric materials are typically orders of magnitude smaller than those of a typical metal substrate, the thickness of the polymer modifier is extremely important. Hence, there is currently a need for an ultra-thin robust hydrophobic modifier that may be applied over a metal surface to enhance heat transfer.

[0010] There is a need for methods and articles/devices for improved heat transfer and/or dropwise condensation of low-surface tension liquids, including hydrocarbon liquids.

Summary of the Invention

[0011] Presented herein are articles and methods featuring substrates with thin, uniform polymeric films grafted thereupon. Techniques such as iCVD allow deposition of precisely-controlled, extremely thin polymeric films on metal substrates, where the polymer is covalently bonded to the substrate. Furthermore, the polymeric film may be crosslinked at or near its exposed surface and/or throughout the bulk of the film via annealing. The resulting coating exhibits significant reductions in thermal resistance, drop shedding size, and degradation rate during dropwise condensation of steam compared to existing coatings.

[0012] Articles and methods presented herein relate to the use of ecofriendly monomers (e.g., 1H, 1H, 2H, 2H – perfluorooctyl acrylate (C6)) for iCVD. C6 monomers undergo surface group reorganization, which is undesirable. Articles and methods presented herein relate to overcoming the surface group organization via crosslinking and/or graded structure. In some embodiments, 1H, 1H, 2H, 2H – perfluorooctyl acrylate as well as C6 monomers with alternative chemistries are deposited via iCVD as precisely-controlled, extremely thin polymeric films on metal substrates, where the polymer becomes covalently bonded to the substrate.

[0013] In some embodiments, the invention relates to an article for enhanced heat transfer, and/or mitigating phase transition and nucleation of undesired materials, and/or reducing adhesion of liquids and solids thereupon, the article comprising a substrate and a (e.g., thin, uniform) polymeric film grafted (e.g., covalently bonded) thereupon.

[0014] In some embodiments, the substrate comprises a metal (e.g., steel, stainless steel, titanium, nickel, copper, aluminum, molybdenum, and/or alloys thereof). In some

embodiments, the substrate comprises a polymer (e.g., polyethylene, polyvinylchloride, polymethylmethacrylate, polyvinylidene fluoride, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, polyisoprene, synthetic rubber, polytetrafluoroethylene, polyethylene terephthalate, acrylate polymer, chlorinated rubber, fluoropolymer, polyamide resin, vinyl resin, expanded polytetrafluoroethylene, low density polyethylene, high density polyethylene, and/or polypropylene). In some embodiments, the substrate comprises a semiconductor and/or ceramic (e.g., SiC, Si, AlN, GaAs, GaN, ZnO, Ge, SiGe, BN, BAs, AlGaAs, TiO₂, TiN, etc.). In some embodiments, the substrate comprises a rare earth element or compound comprising a rare earth element (e.g., a rare earth oxide, carbide, nitride, fluoride, or boride; e.g., cerium oxide CeO₂).

[0015] In some embodiments, the polymeric film comprises a fluoropolymer. In some embodiments, the polymeric film is formed from at least one monomer species comprising one or more pendant perfluorinated alkyl moieties. In some embodiments, the fluoropolymer has at least one CF₃ group. In some embodiments, the fluoropolymer comprises polytetrafluoroethylene (PTFE). In some embodiments, the fluoropolymer comprises [C₁₂H₉F₁₃O₂]_n, where n is an integer greater than zero.

[0016] In some embodiments, the fluoropolymer comprises a member selected from the group consisting of poly(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate), poly(1H, 1H, 2H, 2H - perfluorooctyl acrylate), poly([N-methyl-perfluorohexane-1-sulfonamide] ethyl acrylate), poly([N-methyl-perfluorohexane-1-sulfonamide] ethyl (meth) acrylate), poly(2-(Perfluoro-3-methylbutyl)ethyl methacrylate)), poly(2-[[[2-(perfluorohexyl)ethyl]sulfonyl]methyl]- amino]ethyl]acrylate), poly(2-[[[2-

(perfluoroheptyl)ethyl)sulfonyl]methyl]- amino]ethyl]acrylate), poly(2-[[[2-(perfluorooctyl)ethyl)sulfonyl]methyl]- amino]ethyl]acrylate), and any copolymer thereof.

[0017] In some embodiments, the fluoropolymer is a C6 analog of PFDA. In some embodiments, the fluoropolymer comprises poly(2-(Perfluoro-3-methylbutyl)ethyl methacrylate), or any copolymer comprising 2-(Perfluoro-3-methylbutyl)ethyl methacrylate, wherein the fluoropolymer is crosslinked.

[0018] In some embodiments, the polymeric film comprises at least one member selected from the group consisting of polytetrafluoroethylene (PTFE), poly(perfluorodecylacrylate) (PFDA), polymethylmethacrylate (PMMA), polyglycidylmethacrylate (PGMA), poly-2-hydroxyethylmethacrylate, poly(perfluorononyl acrylate), poly(perfluorooctyl acrylate), and any copolymer thereof. In some embodiments, the polymeric film comprises a copolymer of two or more monomer species.

[0019] In some embodiments, the polymeric film comprises cross-linked polymer and/or cross-linked copolymer. In some embodiments, the polymeric film is cross-linked with a crosslinking agent comprising an organic molecule having at least two vinyl moieties. In some embodiments, the polymeric film is cross-linked with a crosslinking agent comprising at least one member selected from the group consisting of: diethyleneglycol divinyl ether, diethyleneglycol dimethacrylate, diethyleneglycol diacrylate, and/or 1H,1H,6H,6H-perfluorohexyldiacrylate. In some embodiments, the polymeric film is cross-linked with divinyl benzene (DVB). In some embodiments, the polymeric film is cross-linked with a member selected from the group consisting of

ethylene dimethacrylate (EDMA), di(ethyleneglycol)di(methacrylate), di(ethyleneglycol)di(acrylate), ethyleneglycoldimethacrylate (EGDMA), di(ethyleneglycol)di(vinylether) (EDGDVE), and 1H,1H,6H,6H-perfluorohexyldiacrylate.

[0020] In some embodiments, the polymeric film comprises from 0 wt. % to 99 wt.% crosslinking agent (e.g., from 5 wt.% to 90 wt.%; from 15 wt.% to 85 wt.%; from 25 wt.% to 75 wt.%; from 35 wt.% to 65 wt.%; or from 45 wt.% to 55 wt.%).

[0021] In some embodiments, the polymeric film has non-uniform concentration of crosslinking agent along the thickness of the film. In some embodiments, the polymeric film is covalently bonded to the substrate. In some embodiments, the polymeric film is covalently bonded to the substrate by attachment of a vinyl precursor to the substrate, thereby forming a surface comprising a plurality of pendant vinyl moieties. In some embodiments, the vinyl precursor is a member selected from the group consisting of a vinyl functional silane, a vinyl functional phosphonic acid, and a vinyl functional thiol.

[0022] In some embodiments, the vinyl precursor comprises at least one member selected from the group consisting of trichlorovinylsilane, bis(triethoxysilyl)vinylmethylsilane, bis(triethoxysilyl)ethylene, bis(trimethoxysilylmethyl)ethylene, 1,3-[bis(3-triethoxysilylpropyl)polyethylenoxy]-2-methylenepropane, bis[(3-trimethoxysilyl)propyl]-ethylenediamine, bis[3-(triethoxysilyl)propyl]-disulfide, 3-mercaptopropyltrimethoxysilane, and vinyl phosphonic acid.

[0023] In some embodiments, the polymeric film is no greater than 500 nm in thickness (e.g., no greater than 400 nm, no greater than 300 nm, no greater than 200 nm, no greater

than 100 nm, no greater than 75 nm, no greater than 50 nm, no greater than 25 nm, or no greater than 15 nm, e.g., as thin as 10 nm). In some embodiments, the polymeric film comprises a grafting layer (e.g., where the polymeric film is covalently bonded to the substrate) and a bulk film layer (e.g., where the grafting layer has a thickness from about 0.5 nm to about 5 nm, or from about 1 nm to about 3 nm, or from about 1 nm to about 2 nm). In some embodiments, the polymer film has a thickness variation of no greater than about 20% (e.g., no greater than about 15%, no greater than about 10%, or no greater than about 5% -- e.g., the polymer film is uniform).

[0024] In some embodiments, the polymer film has a texture comprising micro- and/or nano-scale features (e.g., ridges, grooves, pores, posts, bumps, and/or protrusions, patterned and/or unpatterned). In some embodiments, the substrate is textured and wherein the polymeric film conforms to the textured substrate surface. In some embodiments, the substrate is textured with micro- and/or nano-scale surface textures (e.g., posts, ridges, cavities, pores, posts, protrusions, etc.). In some embodiments, the polymeric film has a crystalline or semicrystalline surface (e.g., formed via annealing, but not necessarily via annealing).

[0025] In some embodiments, the polymeric film has a surface (e.g., exposed surface) with low contact angle hysteresis (e.g., no greater than 50°, no greater than 40°, no greater than 30°, no greater than 25°, no greater than 20°, no greater than 15°, or no greater than 10°, or no greater than 5°, or no greater than 1° for water; and no greater than 20°, no greater than 15°, no greater than 10°, no greater than 5°, or no greater than 1° for hydrocarbons, refrigerants, cryogenic liquids, and other low-surface tension liquids,

where contact angle hysteresis is the difference between advancing contact angle and receding contact angle).

[0026] In some embodiments, the polymeric film has a surface (e.g., exposed surface) with high advancing contact angle (e.g., no less than 70°, no less than 80°, no less than 90°, no less than 100°, no less than 120°, no less than 130°, no less than 140° for water; and no less than 30°, no less than 40°, no less than 50°, no less than 60°, no less than 70°, no less than 80°, no less than 90°, no less than 100° for hydrocarbons, refrigerants, cryogenic liquids, and other low-surface tension liquids) and/or high receding contact angle (e.g., no less than 60°, no less than 70°, no less than 80°, no less than 90°, no less than 100°, no less than 110°, or no less than 120° for water; and no less than 20°, no less than 30°, no less than 40°, no less than 50°, no less than 60°, no less than 70°, no less than 80°, no less than 90° for hydrocarbons, refrigerants, cryogenic liquids, and other low-surface tension liquids).

[0027] In some embodiments, the article is a condenser (e.g., where dropwise condensation is promoted on the surface of the polymeric film for enhanced heat transfer). In some embodiments, the article is a cooling device for an electronic and/or photonic component (e.g., where heat transfer is promoted from the electronic or photonic component to the surface of the polymeric film, wherein the polymeric film is in contact with the component, and/or wherein the polymeric is in contact with a fluid that is in contact with the component).

[0028] In some embodiments, the article is flexible. In some embodiments, the substrate and the polymeric film grafted thereupon is flexible. In some embodiments, the article is retrofitted to form the grafted polymeric film.

[0029] In another aspect, the invention is directed to a method for using the article described in any of the above embodiments, wherein the method comprises contacting an exposed surface of the polymeric film with a Thermal Interface Material (TIM) (e.g., a thermally conductive material used between microprocessors and heatsinks to increase thermal transfer efficiency).

[0030] In some embodiments, the polymeric film comprises a polymer and/or copolymer, the polymer and/or copolymer comprising at least one perfluorinated pendant chain (e.g., a perfluorinated acrylate and/or a perfluorinated cyclic group, e.g., with 4 to 6 carbons in the ring), a spacer group, and a vinyl-based backbone group.

[0031] In some embodiments, the method includes contacting an exposed surface of the polymeric film with a Thermal Interface Material (TIM) (e.g., a thermally conductive material used between microprocessors and heatsinks to increase thermal transfer efficiency).

[0032] In some embodiments, the invention is directed to a method of preparing an article (e.g., the article described in any of the above embodiments), the method including the step of performing hot wire CVD (HWCVD) to produce the polymeric film grafted on the substrate. In some embodiments, the step of performing HWCVD comprises performing initiated chemical vapor deposition (iCVD) to produce the polymeric film grafted on the substrate.

[0033] In some embodiments, the method further includes the step of annealing the polymeric film by exposure to heat (e.g., to increase crosslinking density and/or degree of crystallinity of the polymeric film). In addition, in some embodiments, annealing can

reduce hysteresis, increase crystallinity at interface, and increase crosslinking at the exposed interface.

[0034] In some embodiments, the HWCVD step is performed to retrofit an existing article (e.g., a condenser, boiler or other heat transfer surface in an HVAC device, a power plant, a desalination plant, a natural gas liquefaction ship, etc.) by grafting the polymeric film upon a surface thereof.

[0035] In some embodiments, the article is a Thermal Interface Material (TIM).

[0036] In some embodiments, the polymeric film has an exposed surface with critical surface energy no greater than 18 mN/m. In some embodiments, the polymeric film has an exposed surface with critical surface energy no greater than 6 mN/m.

[0037] In some embodiments, the polymeric film has an exposed surface with contact angle hysteresis no greater than 25° for water, hydrocarbons, refrigerants, cryogenic liquids, and other heat transfer fluids. In some embodiments, the exposed surface has contact angle hysteresis no greater than 1° or no greater than 5° for water, hydrocarbons, refrigerants, cryogenic liquids, and other heat transfer fluids.

[0038] In some embodiments, the polymeric film has RMS roughness no greater than 100 nm (e.g., no greater than 100 nm, no greater than 75 nm, no greater than 50 nm).

[0039] In some embodiments, the polymeric film provides dropwise condensation and shedding of a hydrocarbon, refrigerant, cryogenic liquid, water, or other low-surface tension liquid. In some embodiments, the hydrocarbon liquid is a member selected from the group consisting of alkanes, alkenes, alkynes, and fuel mixtures (e.g., gasoline, kerosene, diesel, fuel oil); the refrigerant is a member selected from the group consisting of chlorofluorocarbons, hydrofluorocarbons, and hydrochlorofluorocarbons; and the

cryogenic liquid is selected from the group consisting of N₂, O₂, CO₂, He, LNG, methane, butane, propane, and isobutene. In certain embodiments, the hydrocarbon liquid is a member selected from the group consisting of hexane, toluene, isopropanol, ethanol, octane, pentane, and perfluorohexane.

[0040] In some embodiments, the hydrocarbon liquid has surface tension no greater than 30 mN/m (e.g., no greater than 28 mN/m, no greater than 21 mN/m, no greater than 18 mN/m, no greater than 16 mN/m, or no greater than 12 mN/m, or no greater than 6 mN/m).

[0041] In some embodiments, the article is a component (e.g., vessel, pipe, fin, etc.) of a condenser that comes into contact with a condensing liquid (e.g., working fluid). In some embodiments, the article is a component of an oil and/or gas processing apparatus (e.g. fractionation column, liquefaction device). In some embodiments, the article is (or is a component of) a power line, a turbine, an aircraft, a pipeline, a boiler, a windshield, a solar panel, industrial machinery, cookware, a consumer electronic device, a printed circuit board, an electronic component, or a medical device.

[0042] Another aspect discussed herein relates to a method for manufacturing a surface for promoting dropwise condensation and/or shedding of a liquid, the method including the steps of: providing a substrate; and controllably depositing a polymeric film on the substrate via initiated chemical vapor deposition (iCVD).

[0043] In some embodiments, the method includes depositing a vinyl precursor on the substrate prior to, or concurrently with, depositing the polymeric film. In some embodiments, the method includes modulating an average roughness of the deposited layer (e.g., such that roughness is no greater than 100 nm, or no greater than 75 nm, or no

greater than 50 nm). In some embodiments, the modulating includes monitoring a degree of crystallization of the deposited polymeric film; or controlling the proportion of crosslinker; or controlling a temperature of the substrate during deposition; or any combination thereof.

[0044] In some embodiments, the deposited polymeric film has an average thickness from 1 nm to 1 micron. In some embodiments, the deposited polymeric film has an average thickness from 1 nm to 100 nm.

[0045] In some embodiments, the substrate comprises one or more materials selected from the group consisting of a metal (e.g., copper, brass, stainless steel, aluminum, aluminum bronze, nickel, iron, nickel iron aluminum bronze, titanium, scandium, and any alloys thereof), polymer, glass, rubber, silicon, polycarbonate, PVC, ceramic, semiconductor, and any combinations thereof. In some embodiments, the substrate comprises one or more materials selected from the group consisting of plastic, silicon, quartz, woven or non-woven fabric, paper, ceramic, nylon, carbon, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, polyisoprene, synthetic rubber, polytetrafluoroethylene, polyethylene terephthalate, acrylate polymer, chlorinated rubber, fluoropolymer, polyamide resin, vinyl resin, expanded polytetrafluoroethylene, low density polyethylene, high density polyethylene, and polypropylene.

[0046] In some embodiments, the polymeric film has an exposed surface with critical surface energy no greater than 18 mN/m. In some embodiments, the polymeric film has an exposed surface with critical surface energy no greater than 6 mN/m.

[0047] In some embodiments, the polymeric film has an exposed surface with contact angle hysteresis no greater than 25° . In some embodiments, the exposed surface has contact angle hysteresis no greater than 5° for water, hydrocarbons, refrigerants, cryogenic liquids, and other heat transfer fluids, or any combination thereof.

[0048] In some embodiments, the polymeric film has roughness no greater than 100 nm (e.g., no greater than 100 nm, no greater than 75 nm, no greater than 50 nm).

[0049] In some embodiments, the polymeric film provides dropwise condensation and shedding of a hydrocarbon, refrigerant, cryogenic liquid, water, other low-surface tension liquids, or any combination thereof. In some embodiments, the hydrocarbon liquid is a member selected from the group consisting of alkanes, alkenes, alkynes, and fuel mixtures (e.g., gasoline, kerosene, diesel, fuel oil); the refrigerant is a member selected from the group of chlorofluorocarbons, hydrofluorocarbons, and hydrochlorofluorocarbons; and the cryogenic liquid is selected from the group consisting of N₂, O₂, CO₂, LNG, methane, propane, isobutene, and any combination thereof. In some embodiments, the hydrocarbon liquid has surface tension no greater than 30 mN/m (e.g., no greater than 28 mN/m, no greater than 21 mN/m, no greater than 18 mN/m, no greater than 16 mN/m, or no greater than 12 mN/m, or no greater than 6 mN/m).

[0050] Another aspect discussed herein relates to a method of manufacturing the polymeric film on the article of any of the aspects or embodiments discussed above.

[0051] Elements of embodiments described with respect to a given aspect of the invention may be used in various embodiments of another aspect of the invention. For example, it is contemplated that features of dependent claim depending from one

independent claim can be used in apparatus, articles, systems, and/or methods of any of the other independent claims.

Brief Description of the Drawings

[0052] The foregoing and other objects, aspects, features, and advantages of the invention will become more apparent and may be better understood by referring to the following description taken in conjunction with the accompanying drawings, in which:

[0053] Figures 1a-1c illustrate iCVD reactor geometries and reaction processes, in accordance with certain embodiments of the invention. Figure 1b illustrates a schematic of a lab-scale 200 mm diameter iCVD reactor system. For a vinyl homopolymerization, a constant flow of monomer and initiator are metered into the 'pancake' style vacuum reaction chamber. An array of resistively heated wires, suspended a few centimeters above the substrate, heats the vapors. Laser interferometry provides real time monitoring of the iCVD polymer thickness. The pressure of the chamber is controlled by a throttling valve. An unreacted species and volatile reaction by-products are exhausted to a mechanical pump. For copolymerization, an additional monomer feed line would need to be added to the system. Figure 1c shows a schematic cross-section of the iCVD reactor showing decomposition of the initiator by the heated filaments. Surface modification through polymerization of the monomer occurs on the actively cooled substrate.

[0054] Figures 2a-2e illustrate comparison of water condensation on p(PFDA-co-DVB) and fluorosilane coatings deposited on silicon substrates, in accordance with some embodiments of the present invention. Environmental scanning electron micrograph of condensation of pure saturated water vapor at 800 Pa and a supersaturation of $1.16 \pm$

0.05, showing pre-coalescence behavior on copolymer (Figure 2a) and comparing to condensation behavior on fluorosilane (Figure 2b) surfaces, indicating higher nucleation density on copolymer surface. Photographs of condensation of water vapor in air at 40% R.H. on copolymer (Figure 2c) and fluorosilane surfaces (Figure 2d) immediately before and after a shedding event (top and middle photographs, respectively) and 15 seconds after the shedding event (bottom photograph), indicating smaller departing drop diameter on copolymer surface. Figure 2(e) illustrates time-averaged normalized droplet diameter distributions. Smaller drop sizes on copolymer surface indicate better shedding behavior.

[0055] Figures 3a-3e illustrate surface topology and water vapor condensation on p(PFDA-*co*-DVB) coating deposited on an aluminum substrate, in accordance with some embodiments of the present invention. Figure 3a illustrates 50 x 50 μm AFM height scan of surface topology. Dashed box indicates region of the image shown in Figure 3b, 10 x 10 μm AFM height scan of surface topology. Photographs during condensation of saturated steam at 100°C and 101 kPa of prolonged dropwise condensation on grafted coating over a period of 48 hours (Figure 3c) and degradation of fluorosilane coating over a period of 30 min (Figure 3d). Figure 3e illustrates heat transfer coefficient of aluminum substrates with no coating, with a fluorosilane coating, and with a grafted p(PFDA-*co*-DVB) coating, plotted vs. time.

[0056] Figure 4a illustrates dropwise condensation of saturated steam at 6.9 kPa on a copper tube coated with p(PFDA-*co*-DVB). Figure 4b illustrates snapshots immediately before and after a droplet shedding event (left and center photographs, respectively) and 4 hours after shedding event (right photograph).

[0057] Figure 5 (left) illustrates high resolution angle-resolved XPS spectra taken at 0° takeoff angle. Peaks corresponding to -CF₂- and -CF₃ environments are highlighted.

Figure 5 (right) illustrates 10 x 10 μm AFM height scan of surface topology showing spherulitic texture. Dashed box indicates region of (e), 1 x 1 μm AFM phase scan of single roughness feature (bottom) and line height scan (top).

[0058] Figure 6 illustrates the experimental chamber that was used in Dropwise Condensation Experiments.

[0059] Figure 7 illustrates the flow loop of the experimental setup shown in Figure 6.

[0060] Figure 8a illustrates grafted PFDA samples after 1 hour of condensation in saturated steam at 90°C and 70kPa. Figure 8b illustrates ungrafted PFDA sample after 1 hour of condensation in saturated steam at 90°C and 70kPa. Condensate drops on grafted (Figure 8c) and ungrafted (Figure 8d) PFDA surfaces after 10 minutes of condensing saturated steam. The distorted drop shape on the ungrafted sample indicates severe contact line pinning. Departing drop sizes on ungrafted sample were 3.1 mm, compared to 2.3 mm for the grafted surface. Heat transfer coefficient was measured at 31 ± 2 kW/m²K at the beginning of the experiment, and 23 ± 2 kW/m²K after deterioration of ungrafted surface.

[0061] Figure 9 shows AFM images of the poly(1H,1H,2H,2H-perfluorodecyl Acrylate) (pPFDA) homopolymer and different poly(1H,1H,2H,2H-perfluorodecyl Acrylate-copolymer-divinylbenzene) (p(PFDA-co-DVB)) copolymers before and after annealing. The flow rate for each monomer is provided between the brackets.

[0062] Figure 10 is a graph of FT-IR of the pPFDA homopolymer, the pDVB homopolymer and a P(PFDA-co-DVB) copolymer in accordance with some embodiments presented herein.

[0063] Figure 11 shows contact angle measurements using water and mineral oil of the pPFDA homopolymer, the pDVB homopolymer and a series of p(PFDA-co-DVB) copolymers, for non-annealed (left) and annealed (right) samples.

[0064] Figure 12 is a water contact angle graph for pPFDA homopolymer and a series of p(PFDA-co-DVB) copolymers, for non-annealed (solid) and annealed samples (open) in accordance with some embodiments presented herein.

[0065] Figure 13 is a mineral oil contact angle graph for pPFDA homopolymer and a series of p(PFDA-co-DVB) copolymers, for non-annealed (solid) and annealed samples (open) in accordance with some embodiments presented herein.

[0066] Figure 14 illustrates XPS analysis of different p(PFDA-co-DVB) copolymers in accordance with some embodiments presented herein.

[0067] Figure 15 illustrates XRD analysis of the pPFDA homopolymer, the pDVB homopolymer and diverse P(PFDA-co-DVB) copolymer in accordance with some embodiments presented herein.

[0068] Figure 16 illustrates XRD analysis of the pPFDA homopolymer, the pDVB homopolymer and diverse P(PFDA-co-DVB) copolymer after the annealing process in accordance with some embodiments presented herein.

[0069] Figure 17 shows XRD Comparison of pPFDA homopolymer and a series of p(PFDA-co-DVB) copolymer films before and after thermal annealing in accordance with some embodiments presented herein.

[0070] Figure 18 schematically illustrates embodiments employing variation in degree of crosslinking and/or variation in concentration of crosslinking agent as a function of position of the crosslinking agent along the thickness of the polymeric film, in accordance with some embodiments presented herein.

[0071] Figure 19 is a plot showing the effect of contact angle θ on heat transfer coefficient h , where maximum h is at $\theta \sim 90^\circ$ (hexane $66.5/54.6^\circ$), in accordance with some embodiments presented herein.

[0072] Figures 20a and 20b are photographic stills from a video showing dropwise condensation and shedding of *n*-hexane on a PFDA-*co*-DVB on silicon substrate, where $P = 15$ kPa, $T_s = 10 \pm 1^\circ\text{C}$, $T_{\text{sat}} = 18.3^\circ\text{C}$, and $\Delta T = 8.3 \pm 1^\circ\text{C}$, in accordance with some embodiments presented herein.

[0073] Figure 21 is a plot showing FT-IR spectra of eco-friendly pC6PFA homopolymer (a), the pDVB homopolymer (b), and the p(C6PFA-*co*-DVB) copolymer.

[0074] Figure 22 is a plot showing the water contact angles on PTFE, PVDF, and diverse compositional ranges from pC6PFA homopolymer to pDVB homopolymer.

[0075] Figure 23 shows the reorientation, or lack thereof, of pendant perfluorinated pendant groups upon exposure with water. Figure 23a demonstrates how amorphous chains of C6 polymer reorient into the bulk and contribute to high CAH. Figure 23b shows how steric hindrance afforded by DVB crosslinking restricts rearrangement of pendant groups into the bulk of the film, reducing CAH.

[0076] Figure 24 is a plot of the advancing and receding contact angles, along with the contact angle hysteresis, of eco-friendly small-chain perfluorinated films, in accordance with some embodiments presented herein.

[0077] The features and advantages of the present disclosure will become more apparent from the detailed description set forth below when taken in conjunction with the drawings, in which like reference characters identify corresponding elements throughout. In the drawings, like reference numbers generally indicate identical, functionally similar, and/or structurally similar elements.

Description

[0078] It is contemplated that compositions, mixtures, systems, devices, methods, and processes of the claimed invention encompass variations and adaptations developed using information from the embodiments described herein. Adaptation and/or modification of the compositions, mixtures, systems, devices, methods, and processes described herein may be performed by those of ordinary skill in the relevant art.

[0079] Throughout the description, where articles, devices and systems are described as having, including, or comprising specific components, or where processes and methods are described as having, including, or comprising specific steps, it is contemplated that, additionally, there are articles, devices, and systems of the present invention that consist essentially of, or consist of, the recited components, and that there are processes and methods according to the present invention that consist essentially of, or consist of, the recited processing steps.

[0080] Similarly, where articles, devices, mixtures, and compositions are described as having, including, or comprising specific compounds and/or materials, it is contemplated that, additionally, there are articles, devices, mixtures, and compositions of the present

invention that consist essentially of, or consist of, the recited compounds and/or materials.

[0081] It should be understood that the order of steps or order for performing certain actions is immaterial so long as the invention remains operable. Moreover, two or more steps or actions may be conducted simultaneously.

[0082] The mention herein of any publication, for example, in the Background section, is not an admission that the publication serves as prior art with respect to any of the claims presented herein. The Background section is presented for purposes of clarity and is not meant as a description of prior art with respect to any claim.

[0083] Presented herein are articles and methods featuring substrates with thin, uniform polymeric films grafted thereupon. An exposed surface of the film is configured for contact with a liquid, another solid, a vapor, and/or a combined vapor and liquid – that is, there is either a solid-liquid interface, a solid-solid interface, solid-vapor interface, or a solid-vapor/liquid interface at the surface of the grafted polymeric film. The polymeric film may be tuned to have a precise thickness and uniformity. For example, a thickness of less than about 200 nm, less than about 150 nm, less than about 100 nm, less than about 80 nm, less than about 50 nm, less than about 20 nm, or even less than about 10 nm, and the variation of the film thickness of the surface may be less than 20%, less than 15%, less than 10%, or less than 5%.

[0084] Methods are provided herein to graft this uniform polymeric film onto a wide variety of substrate materials. For example, traditional engineering materials such as stainless steel, titanium, nickel, copper, aluminum, magnesium and/or oxides and/or alloys thereof may be coated by a thin conformal film of polymer to obtain a surface that

exhibits robust dropwise condensation. According to some embodiments of the present invention, semiconductors such as Si, SiC, AlN, GaAs, ceramics such as TiN, TiC, SiC, SiN, TiO₂, and rare-earth oxides can be coated as well. Methods are also provided to provide a film with controllable thickness and morphology. For example, in certain embodiments, the film is a conformal film on a textured substrate. In other embodiments, the film is a conformal film on a smooth surface. In other embodiments, the film is a textured film on a smooth surface.

[0085] A film may include or be a thin hydrophobic polymer/copolymer film. Techniques such as initiated chemical vapor deposition (hereafter, “iCVD”) allow deposition of precisely-controlled, extremely thin (e.g., as thin as 10 nm) polymeric films on metal substrates, where the polymer is covalently bonded to the substrate. Furthermore, the polymeric film may be crosslinked at or near its exposed surface and/or throughout the bulk of the film via introduction of a crosslinking agent to the gas stream, and may be followed subsequently by annealing. The resulting film or coating exhibits significant reductions in thermal resistance, drop shedding size, and/or degradation rate during dropwise condensation of steam compared to existing coatings. Certain advantages of the described compositions and methods thereof are detailed as follows.

[0086] Variability of film and substrate composition

[0087] In some embodiments, compositions and methods described herein may have a wide variability of film and substrate materials. Exemplary film materials include, but are not limited to fluoropolymers, including poly-tetrafluoroethylene (PTFE), poly-perfluoroacrylates, poly-perfluormethacrylates, and copolymers thereof. Other exemplary film materials include, but are not limited to, poly-methylmethacrylate (PMMA), poly-

glycidyl methacrylate (PGMA), and poly-2-hydroxyethyl methacrylate. In certain embodiments, the polymeric film includes a fluoropolymer, e.g., PFDA, along with a crosslinker species, e.g., divinylbenzene (DVB). Some embodiments of the present invention utilize a fluorinated polymer, e.g. PTFE or PFDA, or combination thereof. For example, Teflon by DuPont, a PTFE, may be used. Some commercialized films of PTFE are available from GVD (<http://www.gvdcorp.com/>). Such films are described, for example, in U.S. Patent Application Publication No. 2013/0280442, U.S. Patent Application Publication No. 2013/0171546, and U.S. Patent Application Publication No. 2012/0003497, although these films as-described would not be suitable for dropwise condensation owing to high contact angle hysteresis and lack of crosslinking or other means of inducing steric hindrance.

[0088] In certain embodiments, the polymeric film includes exemplary eco-friendly C6-type fluoropolymer materials including, but not limited to 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate, 1H, 1H, 2H, 2H - perfluorooctyl acrylate, 2-(perfluorohexyl) ethyl methacrylate, [N-methyl-perfluorohexane-1-sulfonamide] ethyl acrylate, [N-methyl-perfluorohexane-1-sulfonamide] ethyl (meth) acrylate, 2-(Perfluoro-3-methylbutyl)ethyl methacrylate, 2-[[[2- (perfluorohexyl) ethyl] sulfonyl] methyl]-amino] ethyl] acrylate, and copolymers thereof.

[0089] In addition, 2-(Perfluoro-3-methylbutyl)ethyl methacrylate (C5PFMA), combined with the crosslinking strategy or graded-structure strategy, can be explored via iCVD polymerization. This monomer has enriched CF₃ end groups, which lowers surface energy and promotes hydrophobicity.

[0090] In certain embodiments, the polymeric film comprises at least one member selected from the group consisting of polymethylmethacrylate (PMMA), polyglycidylmethacrylate (PGMA), poly-2-hydroxyethylmethacrylate, polyperfluoroacrylate (PFDA), and copolymers thereof. In certain embodiments, the polymeric film comprises a fluoropolymer. In certain embodiments, the fluoropolymer comprises polytetrafluoroethylene (PTFE). In certain embodiments, the fluoropolymer comprises $[C_{12}H_9F_{13}O_2]_n$, where n is an integer greater than zero (e.g., poly(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate), or 'C6'-analog of PFDA). In certain embodiments, the fluoropolymer comprises a copolymer of divinylbenzene (DVB) and one or both of: PFDA and PTFE.

[0091] In one aspect, the invention is directed to an article for enhanced heat transfer, the article comprising a substrate and a (e.g., thin, uniform) polymeric film grafted (e.g., covalently bonded) thereupon. In certain embodiments, the substrate comprises a metal (e.g., steel, stainless steel, titanium, nickel, copper, and/or alloys thereof). In certain embodiments, the substrate comprises a semiconductor (e.g., SiC, Si, AlN, GaAs, GaN, ZnO, Ge, SiGe, BN, BAs, AlGaAs, TiO_2 , etc.). In certain embodiments, the substrate comprises a rare earth element or compound comprising a rare earth element (e.g., a rare earth oxide, carbide, nitride, fluoride, or boride; e.g., cerium oxide CeO_2).

[0092] In some embodiments, methods are provided herein to graft this uniform polymeric film onto a wide variety of substrate materials. In certain embodiments, the film is a conformal film on a textured substrate. For example, in some embodiments, traditional materials such as stainless steel, titanium, nickel, copper, aluminum and/or their alloys may be coated by a thin conformal film of polymer to obtain a surface that

exhibits robust dropwise condensation. According to some embodiments of the present invention, semiconductors such SiC, AlN, GaAs can be coated as well.

[0093] In some embodiments, the substrate on which the film is deposited includes plastic, silicon, quartz, woven or non-woven fabric, paper, ceramic, nylon, carbon, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, polyisoprene, synthetic rubber, polytetrafluoroethylene, polyethylene terephthalate, acrylate polymer, chlorinated rubber, fluoropolymer, polyamide resin, vinyl resin, expanded polytetrafluoroethylene, low density polyethylene, high density polyethylene, or polypropylene. In some embodiments, the substrate is homogeneous. In some embodiments, the substrate is heterogeneous. In some embodiments, the substrate is planar. In some embodiments, the substrate is non-planar. In some embodiments, the substrate is concave. In some embodiments, the substrate is convex. In some embodiments, the substrate possesses a micro/nanoscale hierarchical texture.

[0094] **Covalent grafting**

[0095] In some embodiments, compositions and methods described herein may have a covalently bonded interface between a film and a substrate. The film-substrate interfaces obtained by other methods of deposition, such as sputtering or casting, suffer from weak bonds between substrate and film. When stressed by the large mismatch in coefficient of thermal expansion ($\Delta\alpha \sim 1 \times 10^{-4}$), hydrolysis in the presence of steam, or the shear stresses encountered during droplet coalescence, these interfaces have been shown to be highly prone to delamination. The covalently bonded interface used in accordance with some embodiments described herein may be shown to resist delamination for prolonged periods. The covalent bonding between the film and the

substrate can also lower the thermal interface resistance, thereby improving the overall heat transfer coefficient.

[0096] Many different chemistries exist for covalently attaching a vinyl or other reactive group to a substrate, and specifically a metal substrate. Silanes, thiols, carboxylic acids, and phosphonates (or phosphonic acids) are examples of such well-known chemistries. Under some conditions, such as alkaline conditions with $\text{pH} > 7$, the hydrolytic stability of phosphonates exceeds that of silanes. Under other conditions, such as under solar irradiation, silanes are more stable than phosphonates. Both phosphonates and silanes can possess one or more vinyl functional group. Silanes with more than one anchor point, referred to as dipodal silanes, result in greater stability and substrate adhesion.

[0097] **Tunable thickness & morphology**

[0098] Previous attempts at promoting dropwise condensation, for example with self-assembled monolayers, have usually resulted in films that degrade over time.

Monolayers will inevitably have holes in the film that will act as degradation initiation sites. For example, the silane-metal bonds of a silanized substrate are susceptible to hydrolysis by steam. Other promoters, such as oleic acids, have been shown to function only on copper substrates, and are incompatible with the more industrially-relevant materials used in heat exchangers such as stainless steel and titanium alloys. A thicker film, e.g., more than a monolayer, will help ensure that there are no regions of exposed substrate.

[0099] However, since the thermal conductivity of polymers are much lower than that of a metal tube (for example, the thermal conductivity of bulk PTFE is approximately

0.25 W/mK as compared to approximately 20 W/mK for stainless steel), previous attempts at obtaining a dropwise promoter surface via polymer films were many microns thick. The additional thermal resistance posed by such thick films was enough to offset any benefits of the higher heat transfer coefficient during dropwise condensation, making these films unusable for promoting dropwise condensation.

[00100] To optimize the film thickness and to ensure that the conduction resistance of the polymer film contributes no more than 1% of the total resistance, the thickness, in some embodiments, must be less than 1 μm . The total thermal resistance includes the following resistances in series: the resistance from the condensing vapor to the substrate, the conduction resistance through the film and the substrate, and the convection resistance of the coolant:

$$R_T = R_s + R_f + R_m + R_w = (1/h_s) + (l_f/k_f) + (l_m/k_m) + (1/h_w) \quad (1)$$

where the subscripts s, f, m , and w represent the steam condensation, film conduction, metal conduction, and water convection, respectively. Typical orders of magnitude of the variables are as follows: $h_s \approx 10^4 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$, $k_f \approx 10^{-1} \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $l_f \approx 10^{-3} \text{ m}$, $k_m \approx 10^2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, $h_w \approx 10^3 \text{ W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$. Thus, the total resistance of the condenser is on the order of $10^{-3} \text{ K}\cdot\text{m}\cdot\text{W}^{-1}$, whereas the conduction resistance due to the film is on the order of $10^{-8} \text{ K}\cdot\text{m}\cdot\text{W}^{-1}$. Since the present coating is so thin (e.g., on the order of 10 nm, 20 nm, 30 nm, 40 nm), it represents only about 0.5% of the condensation resistance and ~0.001% of the total thermal resistance. This is in contrast to the polymer films in conventional systems that were typically many microns thick.

[00101] In some embodiments, a film described herein can be sufficiently thick enough to provide complete coverage, but thin enough to minimize any added thermal

resistance. The thickness of a film may be precisely controlled in real time, for example, by laser interferometry (or other suitable methods) to obtain films as thin as 10 nm. The thermal resistance of a 10 nm film of PTFE is negligible: 4×10^{-8} K/W, corresponding to a thermal conductance of 25 MW/m²K.

[00102] In certain embodiments, the deposited polymeric film has an average thickness from 1 nm to 1 micron. In certain embodiments, the deposited polymeric film has an average thickness from 1 nm to 100 nm.

[00103] In certain embodiments, the polymeric film is no greater than 500 nm in thickness (e.g., no greater than 400 nm, no greater than 300 nm, no greater than 200 nm, no greater than 100 nm, no greater than 75 nm, no greater than 50 nm, no greater than 25 nm, or no greater than 15 nm, e.g., as thin as 10 nm). In certain embodiments, the polymeric film has a thickness variation of no greater than about 20% (e.g., no greater than about 15%, no greater than about 10%, or no greater than about 5% -- e.g., the polymer film is uniform). In some embodiments, the thickness of the polymeric film is about 10 nm, about 20 nm, about 30 nm, about 40 nm, about 50 nm, about 60 nm, about 70 nm, about 80 nm, about 90 nm, about 100 nm, about 125 nm, about 150 nm, about 175 nm, about 200 nm, about 225 nm, about 250 nm, about 275 nm, about 300 nm, about 325 nm, about 350 nm, about 375 nm, about 400 nm, about 425 nm, about 450 nm, about 475 nm, about 500 nm, about 525 nm, about 550 nm, about 575 nm, about 600 nm, about 625 nm, about 650 nm, about 675 nm, about 700 nm, about 725 nm, about 750 nm, about 775 nm, about 800 nm, about 825 nm, about 850 nm, about 875 nm, about 900 nm, about 1000 nm, about 1100 nm, about 1200 nm, about 1300 nm, about 1400 nm, or about 1500 nm.

[00104] Minimizing contact angle hysteresis

[00105] In certain embodiments, a film is particularly useful for enhancing dropwise condensation. The dropwise heat transfer coefficient is strongly influenced by the size of the departing drops. Since a condensate drop begins to present a thermal resistance as soon as it forms, it would be desirable to shed condensate drops as soon as possible. A typical surface will be able to support a drop as it grows to the capillary length, which is approximately 2.7 millimeters for water. At this size, the drops present a significant thermal barrier. If instead the drops can be shed at a much smaller size, the overall heat transfer coefficient will be increased significantly. External forces such as gravity or vapor shear may be utilized to remove condensate droplets, but they will have to overcome the forces due to surface tension that pin the contact line of the drop to the condensing surface. A useful measure of the pinning strength of a surface is the contact angle hysteresis (CAH) – the difference between the advancing and receding contact angles. A lower CAH will result in easier shedding of condensate drops. For smooth surfaces, CAH is minimized when the surface is free of morphological and chemical inhomogeneities. Thus, a smooth, chemically homogeneous surface is desirable for minimizing CAH and maximizing the heat transfer coefficient.

[00106] Additionally, the molecular rearrangement of pendant moieties upon exposure to a wetting fluid such as water gives rise to increased CAH, as explained, for example, in A. Synytska, D. Appelhans, Z. G. Wang, F. Simon, F. Lehmann, M. Stamm, K. Grundke, *Macromolecules* 2007, 40, 1774. This rearrangement may be prevented by increasing the molecular rigidity via adjusting the degree of crystallinity and/or the degree of crosslinking to minimize the contact angle hysteresis. In some embodiments,

compositions and methods described herein may have a tunable molecular rigidity. By altering the deposition parameters, the molecular rigidity may be adjusted at any position (e.g., at any depth or location) within the film, including the film-substrate interface and throughout bulk of the film. At the free surface of the film that is exposed to liquids, it is particularly desirable to obtain rigid films.

[00107] In some embodiments, a film is treated (e.g., annealed) after deposition. Without being bound to any particular theory, annealing can reduce hysteresis, by increasing the degree of crystallinity and/or increasing the degree of crosslinking of the film as explained, for example, in J. L. Yagüe, K. K. Gleason, *Macromolecules*, 2013, 46, 6548.

[00108] For example, a film described according to some embodiments discussed herein may be thermally annealed to improve both durability and contact angle hysteresis (CAH). In experiments described in more detail herein below, copolymer films of poly-perfluorodecyl acrylate and divinylbenzene (PFDA/DVB) were annealed at 60°C to improve crosslinking, resulting in a surface with lower CAH and improved durability in the presence of high-temperature steam.

[00109] The smaller, eco-friendly C₆-type perfluorinated chains are more difficult to restrain from reorientation upon contact with water, but by carefully choosing an appropriate spacer group (located between the acrylate backbone and the fluorinated functional group), this reorientation may be mitigated. For example, a spacer consisting only of an ethyl group, such as (1H 1H 2H 2H C_{n+2}F_{2n+1}) acrylate, crystallization at room temperature is possible only for $n \geq 8$, (for example such as (1H 1H 2H 2H perfluorodecyl) acrylate with $n = 8$), since interactions between adjacent monomers only

occur only between their perfluorinated pendant groups. However, by substituting a [[sulfonyl]methyl]-amino] spacer for the ethyl spacer as an example, additional dipole-dipole interactions between the spacer groups of adjacent monomers are able to further restrain pendant groups and promote crystallization of smaller perfluorinated chains.

Referring now to Figure 23, we find that films of [N-methyl-perfluorohexane-1-sulfonamide] ethyl (meth) acrylate (C6PFSMA) exhibit significantly smaller contact angle hysteresis compared to films of [N-methyl-perfluorohexane-1-sulfonamide] ethyl acrylate (C6PFSA) and Poly(2-(Perfluorohexyl)ethyl methacrylate) (pC6PFMA).

[00110] A polymeric film may be crosslinked to improve rigidity and minimize CAH. Exemplary crosslinkers include, but are not limited to, divinylbenzene (DVB), ethylene dimethacrylate (EDMA), di(ethyleneglycol) di(methacrylate), di(ethyleneglycol) di(acrylate), ethyleneglycoldimethacrylate(EGDMA) and di(ethyleneglycol)di(vinyl ether) (DEGDVE), and/or 1H, 1H, 6H, 6H-perfluorohexyldiacrylate.

[00111] The contact angle hysteresis of iCVD films with various liquids is given in Table 1 below. The contact angle hysteresis may be measured with a goniometer by injecting liquid into a drop to measure the advancing contact angle, and withdrawing liquid from the drop to measure the receding contact angle.

Table 1: Contact angle hysteresis of iCVD films described herein with various liquids

iCVD film	Liquid	$\Delta\theta$ [°]
PFDA homopolymer	Water	5
PFDA homopolymer	Mineral oil	22
PFDA-co-DVB copolymer	Hexane	11
PFDA-co-DVB copolymer	Pentane	8

[00112] In certain embodiments, the polymeric film has a surface (e.g., exposed surface) with low contact angle hysteresis (e.g., no greater than 50°, no greater than 40°,

no greater than 30° , no greater than 25° , no greater than 20° , no greater than 15° , or no greater than 10° for water, where contact angle hysteresis is the difference between advancing contact angle and receding contact angle). In certain embodiments, the polymeric film has a surface (e.g., exposed surface) with high advancing contact angle (e.g., no less than 70° , no less than 80° , no less than 90° , no less than 100° , no less than 120° , no less than 130° for water) and/or high receding contact angle (e.g., no less than 60° , no less than 70° , no less than 80° , no less than 90° , no less than 100° , no less than 110° , or no less than 120° for water). In some embodiments, the advancing water contact angle is greater than about 150° . In some embodiments, the advancing water contact angle is about 150° , about 155° , about 160° , about 165° , or about 170° . In some embodiments, the receding water contact angle is greater than about 150° . In some embodiments, the receding water contact angle is about 150° , about 155° , about 160° , about 165° , or about 170° .

[00113] Preferably, the contact angle hysteresis is $< 25^\circ$. More preferably, the contact angle hysteresis is $< 5^\circ$. If the contact angle hysteresis is higher, it may be compensated for by a lower surface energy, which would result in a larger contact angle and a larger gravitational body force per length of contact line acting to shed the drop.

[00114] In some embodiments, the water contact angle hysteresis is about 10° , about 9° , about 8° , about 7° , about 6° , about 5° , about 4° , or about 3° . In some embodiments, the water contact angle hysteresis is between about 3° and about 10° .

[00115] In some embodiments, the advancing mineral oil contact angle is greater than about 100° . In some embodiments, the advancing mineral oil contact angle is about 100° , about 105° , about 110° , about 115° , about 120° , about 125° , or about 130° . In some

embodiments, the advancing mineral oil contact angle is between about 100° and about 130°.

[00116] In some embodiments, the receding mineral oil contact angle is greater than about 100°. In some embodiments, the receding mineral oil contact angle is about 100°, about 105°, about 110°, about 115°, about 120°, about 125°, or about 130°. In some embodiments, the receding mineral oil contact angle is between about 100° and about 130°.

[00117] In some embodiments, the static mineral oil contact angle is greater than about 100°. In some embodiments, the static mineral oil contact angle is about 100°, about 105°, about 110°, or about 115°. In some embodiments, the static mineral oil contact angle is between about 100° and about 115°.

[00118] iCVD coating process

[00119] Coating typically involves the deposition of films or layers on a surface of a substrate. One manner of effecting the deposition of such films or layers is through chemical vapor deposition (CVD). CVD involves a chemical reaction of vapor phase chemicals or reactants that contain the constituents to be deposited on the substrate. Reactant gases are introduced into a reaction chamber or reactor, and are decomposed and reacted at a heated surface to form the desired film or layer.

[00120] In some embodiments, CVD used in accordance with the present invention is an initiated CVD (iCVD). iCVD Deposition Example in Cylindrical Reactor below discusses a typical experimental set-up for iCVD. In an iCVD process, thin filament wires are heated, thus supplying the energy to fragment a thermally-labile initiator, thereby forming a radical at moderate temperatures. The use of an initiator not only

allows the chemistry to be controlled, but also accelerates film growth and provides control of molecular weight and rate. The energy input is low due to the low filament temperatures, but high growth rates may be achieved. The process progresses independent of the shape or composition of the substrate, is easily scalable, and easily integrated with other processes.

[00121] In certain embodiments, iCVD takes place in a reactor. In certain embodiments, a variety of monomer species may be polymerized and deposited by iCVD. In certain embodiments, the surface to be coated is placed on a stage in the reactor and gaseous precursor molecules are fed into the reactor; the stage may be the bottom of the reactor and not a separate entity. In certain embodiments, a variety of carrier gases are useful in iCVD.

[00122] In certain embodiments, the iCVD reactor has automated electronics to control reactor pressure and to control reactant flow rates. In certain embodiments, unreacted vapors may be exhausted from the system.

[00123] The iCVD process is a single-step, solvent-free, low-energy, vapor-phase method used to deposit conformal films with precisely controllable thickness and in which grafting to the substrate provides enhanced durability, as discussed, for example, in M.E. Alf, A. Asatekin, M.C. Barr, S.H. Baxamusa, H. Chelawat, G. Ozaydin-Ince, C.D. Petruczok, R. Sreenivasan, W.E. Tenhaeff, N.J. Trujillo, S. Vaddiraju, J. Xu, K.K. Gleason, *Adv. Mater.* 2010, 22, 1993. The large choice of suitable monomers that may be used allows for precise design and modulation of surface properties.

[00124] Certain embodiments presented herein relate to films exhibiting a combination of durability and low contact angle hysteresis. Copolymerization with a crosslinker is an

additional method that aids in both further reduction of contact angle hysteresis and also rendering the films more stable to chemical and mechanical degradation – making the films more robust and extending the useful life of those films.

[00125] Certain embodiments presented herein relate to the use of vapor synthesis for copolymerization, which in some embodiments does not require that the two monomers being copolymerized have a common solvent. This characteristic will be recognized by those skilled in the art as a significant advantage over wet-chemistry synthesis techniques, as a common solvent does not exist for PFDA and DVB. In some embodiments, iCVD allows a non-fluorinated crosslinker, DVB, to be readily copolymerized with the fluorinated monomer, PFDA, over its entire compositional range.

[00126] Copolymerization also disrupts crystallization. Since crystallites are one source of roughness, copolymer films in some embodiments may be made to be smoother than crystalline iCVD p(PFDA) homopolymer layers. Such smooth surfaces may be desired to reduce the contact angle hysteresis of low-surface tension fluids such as hydrocarbons, refrigerants, and/or cryogenics. Additionally, the perfluorinated side chains of the PFDA units segregate to the interface under dry conditions in order to minimize surface energy. Surface reconstruction in which the perfluoro chains orient away from the interface can occur when the surface becomes wet.

[00127] The iCVD of homopolymers p(PFDA) and p(DVB) results in highly conformal thin films, and superhydrophobic and superoleophobic surfaces have been demonstrated with iCVD films of p(PFDA).

[00128] Certain embodiments described herein prevent the reorientation of CF₃ groups via crosslinking. A crosslinking agent provides a controllable means of steric hindrance,

because the proportion (e.g., concentration in particular location) of crosslinking agent may be varied along the film thickness. Figure 18 schematically illustrates embodiments employing variation in degree of crosslinking and/or variation in concentration of crosslinking agent as a function of position of the crosslinking agent along the thickness of the polymeric film. The polymeric film includes a grafting layer (e.g., where the grafting layer has a thickness from about 0.5 nm to about 5 nm, or from about 1 nm to about 3 nm, or from about 1 nm to about 2 nm), and a bulk film layer making up the majority (e.g., more than 50%, more than 55%, more than 60%, more than 70%, more than 80%, more than 90%, more than 95%) of the polymeric film. In certain embodiments, the polymeric film has a thickness no greater than 400 nm, no greater than 300 nm, no greater than 200 nm, no greater than 100 nm, no greater than 75 nm, no greater than 50 nm, no greater than 25 nm, or no greater than 15 nm, in thickness. In some embodiments, the polymeric film may be as thin as 10 nm or have a thickness on the order of 10 nm.

[00129] One of the main difficulties in obtaining a surface that exhibits dropwise condensation of hydrocarbons and other low-surface tension liquids has been obtaining a surface with a sufficiently low critical surface tension. The condensate will spread to form a film unless the critical surface tension of the surface is below that of the condensing liquid. Table 2 below lists the surface tension values for water and a variety of other liquids, including *n*-alkanes (octane, hexane, pentane) and a fluorocarbon similar to a typical refrigerant. Table 3 lists refrigerants, e.g., hydrofluorocarbons, chlorofluorocarbons, and hydrochlorofluorocarbons.

[00130] The *n*-alkanes have surface tensions that are considerably lower than water, and also lower than most common industrial materials (including polymers) whose critical surface tensions are shown in Table 4. For example, Teflon has a surface energy of 19 mN/m, since it is composed principally of CF₂ groups, and is not sufficient to condense hexane or lower alkanes. Even trichloro(1H,1H,2H,2H-perfluorooctyl)silane (commonly referred to as fluorosilane, a low-surface energy fluorinated silane surface modifier), has a critical surface energy of 10 mN/m. Although fluorosilane is terminated by CF₃ groups, the lack of crosslinking or other steric hindrance allows these CF₃ group to reorient in the presence of water or another wetting liquid. As a result, it is difficult to obtain a surface with a critical surface energy low enough to promote dropwise condensation of these liquids.

Table 2: Surface tensions of water and various low-surface tension fluids.

liquid	σ_{lv} @25°C [mN/m]
water	72.71
toluene	27.93
isopropanol	20.92
ethanol	24.77
octane	21.08
hexane	17.98
pentane	15.47
perfluorohexane	11.47

Table 3: List of refrigerants.

Chlorofluorocarbons

R-11 Trichlorofluoromethane
R-12 Dichlorodifluoromethane
R-13 Chlorotrifluoromethane
R-13B1 Bromotrifluoromethane

R-14 Tetrafluoromethane
 R-113 Trichlorotrifluoroethane
 R-114 1,2-Dichloro-1,1,2,2-Tetrafluoroethane
 R-500 Dichlorodifluoromethane, Difluoroethane
 R-502 Chlorodifluoromethane, Chloropentafluoroethane
 R-503 Chlorotrifluoromethane, Trifluoromethane

Hydrochlorofluorocarbons

R-12 1-Chloro-1,2,2,2-tetrafluoroethane, 1,1,1,2-Tetrafluoroethane
 R-22 Chlorodifluoromethane
 R-123 Dichlorotrifluoroethane
 R-124 1-Chloro-1,2,2,2-Tetrafluoroethane
 R-401A Chlorodifluoromethane, Chlorotetrafluoroethane
 R-401B Chlorodifluoromethane, Chlorotetrafluoroethane
 R-402A Chlorodifluoromethane, Pentafluoroethane
 R-402B Chlorodifluoromethane, Pentafluoroethane
 R-408A Trifluoroethane, Chlorodifluoromethane
 R-409A Chlorodifluoromethane, Chlorotetrafluoroethane
 R-412A Chlorodifluoromethane, 1-Chloro-1,1-Difluoroethane and
 Octafluoropropane
 R-414B Chlorodifluoromethane, Chlorodifluoroethane, Chlorotetrafluoroethane
 R-416A 1-Chloro-1,2,2,2-tetrafluoroethane, 1,1,1,2-Tetrafluoroethane

Hydrofluorocarbons

R-23 Trifluoromethane
 R-116 Hexafluoroethane
 R-134a 1,1,1,2-Tetrafluoroethane
 R-404A Pentafluoroethane, 1,1,1,2-Tetrafluoroethane, Trifluoroethane
 R-407A Difluoromethane, Pentafluoroethane, 1,1,1,2-Tetrafluoroethane
 R-407B Difluoromethane, Pentafluoroethane, 1,1,1,2-Tetrafluoroethane
 R-407C Difluoromethane, Pentafluoroethane, 1,1,1,2-Tetrafluoroethane
 R-410A Pentafluoroethane, Difluoromethane
 R-417A 1,1,1,2-Tetrafluoroethane and Pentafluoroethane
 R-422A 1,1,1,2-Tetrafluoroethane and Pentafluoroethane
 R-422D 1,1,1,2-Tetrafluoroethane and Pentafluoroethane
 R-423A Tetrafluoroethane, Heptafluoropropane
 R-427A 1,1,1,2-Tetrafluoroethane, Pentafluoroethane
 R-438A Difluoromethane, Pentafluoroethane, 1,1,1, 2-Tetrafluoroethane, n-
 Butane, Isopentane
 R-507 Pentafluoroethane, Trifluoroethane
 R-508A Trifluoromethane, Hexafluoroethane
 R-508B Trifluoromethane, Hexafluoroethane

Table 4: Critical surface energy of industrial polymers.

Polymer abbr.	Polymer Name	Surface Energy (dynes/cm)	Contact Angles (degrees)
PES	Polyethersulfone	46	90
	Styrene butadiene rubber	48	
PPO	Polyphenylene oxide	47	75
	Nylon 6/6 (polyhexamethylene adipamide)	46	
PC	Polycarbonate	46	75
	Nylon-6 (polycaprolactam)	38	
PET	Polyethylene terephthalate	42	76
PMMA	Polymethylmethacrylate	41	82
SAN	Styrene acrylonitrile	40	74
	Polyimide	40	83
PVC r	Polyvinyl chloride, rigid	39	90
	Polyester	41	70
	Acetal	36	85
ABS	Acrylonitrile butadiene styrene	35	82
PPS	Polyphenylene sulfide	38	87
PVA	Polyvinyl alcohol	37	10
	Polyacrylate (acrylic film)	35	
PVC p	Polyvinyl chloride, plasticized	35	89
PS	Polystyrene	34	72
	Nylon-12	36	
	Surlyn ionomer	33	80
PBT	Polybutylene terephthalate	32	88
CTFE	Polychlorotrifluoroethylene	31	
PP	Polypropylene	30	88
PU	Polyurethane	38	85
PE	Polyethylene	30	88
PVF	Polyvinyl fluoride	28	
PVDF	Polyvinylidene fluoride	25	80
	Natural rubber	24	
PDMS	Polydimethyl siloxane (silicone elastomer)	23	98
FEP	Fluorinated ethylene propylene	20	98
PTFE	Polytetrafluoroethylene	19	120

[00131] Even if a surface can be found with sufficiently low surface energy to avoid spreading of the condensate, a second difficulty in obtaining dropwise condensation of low surface tension liquids is reducing the contact angle hysteresis (and thus the drop adhesion). If the adhesion of the condensate drops to the surface is high, then the drops will be unable to shed from the surface, and the initial dropwise condensation will proceed until the individual drops merge to form a continuous film. This is an especially difficult problem in the case of low-surface tension fluids. Since the contact angle of a condensate drop will inevitably be low (in the range of about 10° to 30°), the ratio of the

body force due to gravity acting to shed the drop will be small compared to the force acting to pin the drop to the surface. A plot showing the effect of contact angle θ on heat transfer coefficient h is shown in Figure 19, where maximum h for water is at $\theta \sim 90^\circ$ and for octane $\sim 50^\circ$.

[00132] Surfaces that promote dropwise shedding of low-surface tension condensates, such as liquid hydrocarbons, are demonstrated in the experimental examples presented herein. For example, demonstrated herein is the dropwise condensation of hexane on a surface comprising iCVD copolymer of PFDA-*co*-DVB. Figures 22A and 22B are photographic stills from a video showing dropwise condensation and shedding of *n*-hexane on a PFDA-*co*-DVB on silicon substrate, where $P = 15 \text{ kPa}$, $T_s = 10 \pm 1^\circ\text{C}$, $T_{\text{sat}} = 18.3^\circ\text{C}$, and $\Delta T = 8.3 \pm 1^\circ\text{C}$.

[00133] Surfaces such as the ones shown in Figures 20a and 20b have valuable applications in a wide variety of industries, for example, in applications of refrigeration, dehumidification, and HVAC, which condense a refrigerant, generally a low-surface tension fluorocarbon fluid. Condensers that promote dropwise shedding of such fluids result in higher overall efficiencies and/or lower device footprint. Further applications include power plants utilizing organic Rankine cycles, e.g., with isobutene, pentane, or propane as the working fluid, which may allow for smaller condensers to be used, and lower capital costs for such power plants. Other applications include the fractionation of hydrocarbon crude streams into constituent components, allowing for smaller fractionation columns with fewer stacks.

[00134] Also presented herein is the finding that surfaces with both (1) low critical surface energy and (2) low contact angle hysteresis promote dropwise shedding of low-

surface tension condensates such as liquid hydrocarbons. Furthermore, owing to the grafting (e.g., covalent bonding) of the film to the substrate, these surfaces display a high degree of robustness. They are seen to survive prolonged condensation in 100°C steam with no noticeable degradation.

[00135] For example, the critical surface energy of an iCVD-grafted PFDA homopolymer has been determined to be 5.6 mN/m, as compared to 18.5 mN/m for the ungrafted homopolymer. Critical surface energy may be determined by plotting $1 - \cos(\theta_a)$, where θ_a is the cosine of the advancing contact angle of a homologous series of liquids, e.g. n-heptane, n-octane, n-decane, etc., and finding the x-intercept. In certain embodiments, the critical surface energy is < 18 mN/m. If the critical surface energy is higher, the surface may become flooded by the low-surface tension fluid. In some embodiments, the critical surface energy is < 6 mN/m.

[00136] There is a wide array of industrial applications for iCVD coatings for dropwise condensation and shedding of low-surface tension liquids. Condensation of low-surface tension liquids in industrial applications has occurred in the filmwise mode due to the aforementioned difficulties in achieving dropwise condensation and shedding. As a result, since the thermal conductivities of low-surface tension fluids (typically < 0.2 W/mK) are worse even than water (0.6 W/mK), these condensers suffer from considerable thermal inefficiencies due to the thermal resistance of the condensate film. By implementing a dropwise condenser, e.g., with iCVD coating as described herein, the heat transfer coefficient [W/m²K] can increase tenfold. Thus, in certain embodiments, for a given coolant temperature, ten times the heat can be transferred, or the same amount

of heat can be transferred by a heat exchanger that is smaller than the original size or by a temperature difference that is smaller than the original temperature difference.

[00137] The coatings/surfaces described herein have numerous important uses in oil and gas processing (e.g., LNG, propane, etc.); refrigerants, condenser coils in dehumidification systems, commercial/residential HVAC, consumer packaging, medical devices, water recovery from cooling towers, dew/fog collection, organic Rankine cycles, steam based power generation (e.g., solar thermal, geothermal, etc.), liquefaction (including LNG, CO₂, N₂, liquid oxygen, etc.), and phase transition applications involving mitigation of icing, hydrates, and scale formation.

[00138] In applications of refrigeration, dehumidification, and HVAC which condense a refrigerant (typically a low-surface tension fluorocarbon fluid), dropwise condensers would result in higher overall efficiencies and lower device footprint. In power applications utilizing organic Rankine cycles, e.g. with isobutene, pentane, or propane as the working fluid, condensers must be used to pull the working fluid through the turbine and condense back to liquid to be pumped back through the cycle. Implementing dropwise condensers would allow for smaller equipment size, which would significantly reduce the capital cost of such plants; and would also allow for better overall cycle efficiencies. In the fractionation of crude streams into constituent components, e.g. kerosene, alkanes, fuel oils, and diesel and heavier fuels, dropwise condensing surfaces would allow for smaller fractionation columns with fewer stacks. In applications such as the liquefaction of natural gas, oxygen, and nitrogen, cold boxes are used to condense a gas stream into a liquid. The cooling flux of the cold box is provided by a portion of the liquefied product, and so by increasing the heat transfer coefficient of the condensers, the

liquefaction plant would be able to produce a larger amount of valuable liquid product instead of less-valuable gaseous product. Furthermore, with the advent of ship-based liquefaction plants, the heat transfer equipment becomes severely space-constrained. A dropwise condenser would provide the same heat flux in a much smaller footprint than the current filmwise condensers.

[00139] Industrial applications of the surfaces described herein include phase change applications, wherein the surfaces minimize adhesion of solid phases nucleating and growing on the surfaces, e.g., where there is ice formation on power lines, wind turbines, aircraft, and municipal pipelines; where there is hydrate formation on oil and gas equipment (e.g., undersea); and where there is scale formation on equipment in power plants and boilers, in desalination plants, and municipal pipelines. The low hysteresis of the coatings/surfaces described herein can be exploited for shedding (e.g., dropwise shedding) of unwanted liquid drops, as in water from car windshields, solar panels, and industrial machinery; oil contaminants from household cookware, consumer electronics, and industrial machinery; and blood and other biological fluids from medical devices. The low surface energy of the coating/surfaces described herein can also be exploited for their low solid-solid frictional properties, e.g., sliding linear bearings, bushings, and non-stick household implements.

[00140] In certain embodiments, a film described herein is used in power plants, desalination condensers, humidification-dehumidification systems, or heating, ventilation, and air conditioning (HVAC). In certain embodiments, a film is used in a thermal interface material (TIM) because of its covalent bonding and flexibility. In certain embodiments, a film is used for cooling of electronics and photonics.

[00141] In certain embodiments, the surface energy of a thin film (e.g., a film of fluorinated polymer) is sufficiently low to be oleophobic, which would allow it to be used for dropwise condensation of hydrocarbons.

[00142] Appendix A discusses sustained dropwise condensation of steam on a thin film of poly-(1H,1H,2H,2H-perfluorodecyl acrylate)-*co*-divinyl benzene (p(PFDA-*co*-DVB)).

[00143] It is found that roughness can be precisely specified and designed so that it is high enough to enhance nucleation density but low enough such that it does not adversely affect hysteresis. Roughness may be designed by numerous methods, including, for example, degree of crystallization, extent of crosslinking, composition of crosslinker, and substrate temperature during deposition.

[00144] Also described herein are findings regarding variables of the described coatings/surfaces, including surface energy, roughness, and substrate bonding.

[00145] Regarding surface energy, it is found that the surface energy of the surface/coating should be lower than the condensate liquid. For example, for the PFDA-*co*-DVB copolymer described herein, surface energy may be determined from a ratio of CF₃ groups to CF₂ groups at the surface, where $\sigma_{\text{CF}_3} = 6 \text{ mN/m}$ and $\sigma_{\text{CF}_2} = 18 \text{ mN/m}$. It is found that on a non-crosslinked surface (e.g., fluorosilane), CF₃ groups re-orient away from the surface when exposed to water. It is also found that DVB crosslinking rigidifies the CF₃ groups of the PFDA and prevents reorientation. Furthermore, it is found that grafting forces orientation of CF₃ groups toward the surface.

[00146] Regarding roughness, it is found that roughness should be low enough to avoid contact angle hysteresis. For example, roughness features small than ~100 nm are

“weak” defects and do not contribute to hysteresis. It is also found that some small amount of roughness is beneficial for providing nucleation sites. Moreover, roughness can be controlled by crosslinking. For example, PFDA homopolymer (non-crosslinked) crystallizes into large hemispherical agglomerations. Crosslinking prevents crystallization and lowers roughness. Copolymer films of p(PFDA-co-DVB) exhibit a much smaller degree of crystallinity than PFDA homopolymer, however still exhibit semicrystalline agglomerations that enhance the nucleation density.

[00147] Regarding substrate bonding, it is found that covalent bonds of the present coatings/surfaces are stronger than van der Waals bonds of typical Teflon coatings. Moreover, the vinyl group of PFDA is found to bond covalently with an initiated vinyl group on the surface.

Experimental Examples

iCVD Deposition Experiment A – p(PFDA-co-DVB)

[00148] In this Example, polymerizations were conducted in a custom-design cylindrical reactor (diameter 24.6 cm and height 3.8 cm). On top of the reactor laid a quartz top that allowed laser interferometry (633-nm He-Ne laser, JDS Uniphase) for in-situ film thickness monitoring. Inside the reactor, 14 parallel ChromAlloy filaments (Goodfellow) were resistively heated at 230°C and the stage was back-cooled at a constant temperature of 30°C by water using a recirculating chiller/heater (Neslab RTE-7). Reactor pressure was maintained at 200 mTorr using a throttle valve (MKS Instruments). The radical initiator, and the gas carrier were delivered inside the reactor through mass flow controllers (MKS Instruments). The fluorinated PFDA monomer and the DVB cross-linker were heated in a glass jar to a temperature of 80 °C and 60 °C

respectively, and their flows were controlled by needle valves. The flow rates of initiator and monomer were kept constant at 3.2 and 0.2 sccm. For the different experiments, the flow rate of cross-linker was varied to 0, 0.2, 0.6 and 1 sccm, and a patch flow of gas carrier was introduced to keep a total flow of 5 sccm. Thickness samples ranged from 10 nm to 3 μm . Figure 10 shows incorporation of DVB in the copolymer film.

iCVD Deposition Experiment B – grafted p(PFDA-co-DVB)

[00149] To deposit a silane adhesion layer prior to grafted iCVD polymerization, substrates were first cleaned by sonication in acetone for 5 minutes, followed by rinsing in DI water (18 M Ω m), followed by sonication in isopropanol for 5 minutes, and finally a rinse with DI water. The surfaces were treated with oxygen plasma for 10 minutes for further cleaning and for creating surface hydroxyl groups. After plasma treatment, the surfaces were immediately placed in a vacuum desiccator along a small open vial containing 100 μL of either trichlorovinylsilane (97%, Sigma Aldrich) as a grafting precursor for the polymer films. The chamber was pumped down to 200 mTorr, and the chamber was isolated to allow the silane to vaporize. The chamber was purged twice more, then isolated. The silane was allowed to vaporize and react with the substrate for 2 hours. After deposition, the surfaces were sonicated in toluene to remove excess unreacted silane and rinsed with DI water.

[00150] iCVD polymerizations were conducted in a custom-design cylindrical reactor (diameter 24.6 cm and height 3.8 cm), supporting an array of 14 parallel chromoalloy filaments (Goodfellow) suspended 2 cm from the stage. Tert-butyl peroxide (TBPO) (98%, Aldrich), PFDA (97%, Aldrich), and DVB (80%, Aldrich) were used as received. The peroxide initiator, TBPO, was delivered into the reactor through a mass flow

controller (MKS Instruments) at a constant flow rate of 3.2 sccm. PFDA and DVB were vaporized in glass jars that were heated to 80 and 60°C, respectively. The flow rates were controlled using needle valves and kept constant at 0.2 and 0.6 sccm. The filaments were resistively heated to 230°C using a DC power supply (Sorensen), and the temperature was measured by a K-type thermocouple (Omega Engineering). The sample stage was backcooled at 30°C using a recirculating chiller/heater (Neslab RTE-7). The working pressure was maintained at 200 mTorr using a throttle valve (MKS Instruments). The reactor was covered with a quartz top (2.5 cm) that allowed for in-situ thickness monitoring by interferometry with a 633 nm HeNe laser source (JDS Uniphase). Final thickness of the copolymer deposited on the metal substrate corresponded to 40 nm. Afterwards, a thermal annealing process was performed by introducing the sample in an oven (VWR) at 80°C for 30 min. The full width at half-maximum (FWHM) was fixed at 2–3 eV to take into account the broadening of the 1 eV electron beam, while using XPS Scienta Database F1s peaks with FWHM of 2 eV.

iCVD Deposition Experiment C – Annealing

[00151] This Example characterizes samples that were prepared via iCVD deposition of p(PFDA-co-DVB) on silicon substrates before and after annealing. iCVD films were prepared in the same manner described in iCVD Deposition Example – p(PFDA-co-DVB), and then further characterized by AFM. After iCVD deposition, samples were annealed in a furnace at 80 °C for 30 min and characterized again by AFM. Referring now to Figure 9, we observe that after annealing, the quadratic mean roughness of all surfaces decreases, indicating an increase in the degree of crystallinity in the case of the PFDA homopolymer and an increase in the degree of crosslinking in the cases of the

DVB-crosslinked copolymers. Referring now to Figure 17 showing a comparison of XRD spectra of PFDA homopolymer and p(PFDA-co-DVB) films before and after thermal annealing, we also observe an increase in the degree of crystallinity of PFDA homopolymer as evidenced by the increased area under the curve corresponding to intensity vs. 2θ , and a decrease in degree of crystallinity of the crosslinked polymers as evidenced by a decrease in the area under the curve corresponding to intensity vs. 2θ .

iCVD Deposition Experiment D – eco-friendly pC6PFA-co-DVB

[00152] In this Example, films of varying compositional ranges of 1H, 1H, 2H, 2H - perfluorooctyl acrylate) (pC6PFA;C6) and divinylbenzene (DVB) were deposited via iCVD on silicon wafer substrates. Flowrates of monomer and initiator species and nitrogen patch flow are indicated in Table 5 below.

Table 5: Nomenclature and flow rates of precursors

Sample	Flow rate (sccm)			
	C6PFA	DVB	TBPO	N ₂
C0	0.2	0	1.2	1.6
C1	0.2	0.2	1.2	1.4
C2	0.2	0.4	1.2	1.2
C3	0.2	0.6	1.2	1
C4	0.2	1	1.2	0.6

[00153] The Fourier transform infrared spectroscopy (FT-IR) spectra of the films are shown in Figure 21. pC6PFA homopolymer gives a sharp band due to carbonyl group at 1743 cm^{-1} . The two bands at 1237 and 1204 cm^{-1} are caused by the asymmetric and

symmetric stretching of the $-\text{CF}_2-$ moiety, respectively. The sharp band at 1146 cm^{-1} is caused by the $-\text{CF}_2-\text{CF}_3$ end group. The pDVB homopolymer FT-IR spectrum shows the $-\text{CH}_2-$ stretching bands at 2871 cm^{-1} , confirming the formation of backbone. The aromatic $-\text{CH}-$ contribute to bands between 3000 and 3100 cm^{-1} . The bands between 700 and 1000 cm^{-1} are characteristics of substituted phenyl groups. The band at 903 cm^{-1} results from unreacted vinyl groups. The copolymer presents all the characteristic bands associated with its components. The FT-IR results show the incorporation of the two monomers into the copolymer film and the retention of the chemical functionality from both reactants after the polymerization.

[00154] The effects of DVB crosslinking on CAH were studied by WCA measurements (Figure 22). pC6PFA homopolymer film presents high static WCA and advancing WCA, but low receding WCA. This behavior of pC6PFA surface has been well explained: in its dry state, the fluoroalkyl side chains orient to the outermost surface layer due to phase segregation between hydrogenated and fluorinated moieties. Surface reorganization occurs in presence of water, leading to surface exposure of hydrophilic moieties. The reconstruction easily happens because pC6PFA is unable to form crystalline structure. In contrast, p(C6PFA-co-DVB) films show improved dynamic water repellency. The receding WCA of all copolymer films are significantly enhanced. The movement of water front can be affected by surface roughness, heterogeneity, reorientation, and mobility. The AFM observation of films shows that the differences in roughness are not significant enough to influence the WCA hysteresis. Therefore the results suggest that the crosslinking of DVB units hinders the reorientation of surface fluorine groups. It is hypothesized here that the DVB units have two effects, on main

chain and side chain respectively, contributing to the restrain of fluorine groups (Fig. X): first, the rigid crosslinker can reduce the flexibility of main chain, reducing the T_g ; second, the planar crosslinker can sterically mitigate side chain reconstruction by reducing free volume.

Film Deposition Experiment – effect of spacer groups

[00155] Do demonstrate the ability of the spacer group to affect the rigidity and thus

CAH of deposited films, thin films of 1H, 1H, 2H, 2H - perfluorooctyl acrylate

(C6PFA)Poly(2-(Perfluorohexyl)ethyl methacrylate) (pC6PFMA) [N-methyl-

perfluorohexane-1-sulfonamide] ethyl acrylate (C6PFSA) and [N-methyl-

perfluorohexane-1-sulfonamide] ethyl (meth) acrylate (C6PFSMA) were spin-coated

onto silicon substrates. Advancing and receding contact angles and CAH are shown in

Figure 24, indicating that the additional dipole-dipole interactions afforded by the spacer

group of pC6PFSMA act to significantly reduce the CAH as compared to pC6PFA as

shown in Figure 23.

Film Characterization Experiment A – XPS Spectra

[00156] Figure 5 (left) shows the high-resolution C1s X-ray photoelectron spectra

(XPS) of the iCVD p(PFDA-*co*-DVB) copolymer surface. The pendant groups from the

PFDA consist of -CF₂- and -CF₃- and these two bonding environments can be readily

resolved at 290.8 and 293.1 eV, respectively. In aggregate, these fluorinated carbon

groups account for $61.8 \pm 0.4\%$ of the area of the spectrum. The assignments at lower

binding energies represent carbon items directly bonded only to oxygen, hydrogen, or

other carbon atoms. However, the precise assignments of the peaks at lower binding

energy is ambiguous due to the multitude of environments arising from the main acrylate

portion of the PFDA and from the DVB.

[00157] The $-\text{CF}_2-$ and $-\text{CF}_3-$ bonding environments were previously observed in C1s XPS spectrum of the iCVD PFDA homopolymer, representing a combined area of $61.4 \pm 0.3\%$ and in agreement with the structural formula for PFDA which gives a theoretical value of 61.5%. The similarity with homopolymer results suggests the degree of DVB crosslinker incorporation in the copolymer in the near-surface region probed by XPS is quite low. Thus, the surface properties of the copolymer in the dry state, such as the advancing contact angle, will be dominated by the PFDA units. When examined by Fourier transform infrared spectra (FTIR), which penetrates the entire film thickness, sp^2 C-H stretching modes between 2810 and 2890 cm^{-1} were observed, confirming the incorporation of the DVB in the bulk of the film. These underlying crosslinking units are anticipated to reduce the ability of the surface layer to reconstruct between the dry and wet states, potentially reducing this contribution to contact angle hysteresis. By following a deposition of PFDA:DVB 0.2:0.6 sccm with a thermal annealing step, the advancing and receding water contact angles on the resultant thin film are $132^\circ \pm 1^\circ$ and $127^\circ \pm 1^\circ$, respectively, with a CAH of 5° . Average film thicknesses were measured by ellipsometry, AFM, and contact profilometry to be $41.5 \pm 2.4 \text{ nm}$. AFM scans (Figures 1d and 1e) illustrate that the surface is covered by structures with a height of ca. 100 nm and an average spacing of $1.3 \pm 0.7 \text{ }\mu\text{m}$, resulting in an RMS roughness of 75 nm. These rough features are semicrystalline aggregates formed at nucleation sites during the condensation polymerization reaction of the monomers.

[00158] Previous literature has shown that $-(\text{CF}_2)_n\text{CF}_3$ chains with $n \geq$ leads to aggregates in a smectic B structure that arrange into a rotationally symmetric fiber texture. On the other hand, the fluorosilane surface, which is composed of larger, less

sterically-hindered functional groups with a thickness of 2.5 nm and an RMS roughness of 1.5 ± 0.3 nm, exhibited a CAH of $25^\circ \pm 3^\circ$. Since the roughness of the silanized surface is lower than that of the copolymer surface, morphology alone cannot explain the lower hysteresis of the copolymer surface. Instead, this may be attributed to the steric hindrance induced by the crosslinking that prevents the $-\text{CF}_3$ groups from shifting away from their low-energy unwetted state.

Film Characterization Experiment B - Film Thickness Measurements

[00159] Film thicknesses were measured with variable-angle ellipsometric spectroscopy (VASE, M-2000, J. A. Woollam) and by measuring scratch step height with atomic force microscopy (AFM, MP3D-SA, Asylum) and contact profilometry (Model 150, Dektak). All VASE thickness measurements were performed at a 70° incidence angle using 190 different wavelengths from 315 to 718 nm. A nonlinear least-squares minimization was used to fit ellipsometric data of dry films to the Cauchy-Urbach model. The thickness was obtained upon convergence of the algorithm. FTIR measurements were performed on a Nicolet Nexus 870 ESP spectrometer in normal transmission mode equipped with a MCT (mercury cadmium tellurium detector and KBr beamsplitter). Spectra were acquired over the range of 400 to 4000 cm^{-1} with a 4 cm^{-1} resolution for 256 scans. All AFM thickness measurements were performed in tapping mode over an area of $20\text{ }\mu\text{m} \times 20\text{ }\mu\text{m}$ using a cantilever with a tip radius of 9 ± 2 nm (AC200TS, Asylum). The film thickness was calculated as the difference between the average heights of the rough film surface and the trough of the scratch; the rough built-up edge of the scratch was masked from analysis. The profilometry measurements were performed with a stylus having a radius of $12.5\text{ }\mu\text{m}$. The film thickness was similarly calculated as the

difference in the average height of the rough film and the smooth scratch trough. AFM and profilometry measurements were repeated on at least four locations. Film thickness is reported as the mean and standard deviation of all measurements.

Film Characterization Experiment C - Surface Roughness Measurements

[00160] Surface roughness was measured using atomic force microscopy (AFM, MP3D-SA, Asylum) in tapping mode. The advancing and receding contact angles were measured using a goniometer (Model 590 Advanced, ramé-hart). The hysteresis was also measured during condensation on the grafted polymer sample as the difference between the receding and advancing ends of a drop immediately before departure. Contact angles during condensation on the silanized sample could not be measured due to the film covering the surface.

Dropwise Condensation Experiment A – Nucleation and Shedding Comparison

[00161] In addition to CAH, the dropwise condensation heat transfer depends on a number of complex factors including nucleation site density and population distribution. To investigate the behavior of these surfaces during condensation, saturated pure water vapor at 800 Pa was condensed while cooling the surface with a Peltier device to a supersaturation of 1.16 ± 0.05 and imaging with an environmental scanning electron microscope (ESEM). 2 mm x 2 mm sample substrates were secured to an aluminum stub with double-sided carbon adhesive and instrumented with a K-type thermocouple embedded into the tape. The aluminum stub was clamped into a Peltier cooling stage (Coolstage Mk 2, Deben) which was attached to the stage of an environmental scanning electron microscope (EVO 55, Zeiss). The chamber was purged with water vapor three times up to 3 kPa and down to 10 Pa to remove non-condensable gases. After purging,

the pressure was held at 800 Pa, and the temperature was slowly decreased at a rate of 0.5 K min⁻¹ until formation of observable water droplets (>1 μm diameter). Accelerating voltage was 20 kV and beam current was 100 nA. Images were recorded at ca. 1Hz, and the stage was moved to different areas to avoid charging effects on nucleation.

Nucleation densities were measured as the mean and standard deviation of at least five different locations on each surface. During the pre-coalescence growth regime, it was observed that the nucleation density on a p(PFDA-co-DVB) surface ($173 \pm 19 \text{ mm}^{-2}$, as shown in Figure 2a) was significantly higher than that on a fluorosilane surface ($110 \pm 10 \text{ mm}^{-2}$, as shown in Figure 2b) – owing at least in part to the rougher surface providing a larger number of concavities that act as nucleation sites. During condensation of an air stream saturated with water vapor under ambient conditions (21°C, 40% relative humidity), the departing diameter was $2.0 \pm 0.3 \text{ mm}$ (as illustrated in Figure 2c). This is considerably smaller than the departing drop sizes on other common hydrophobic modifiers such as gold (3.3 mm) and oleic acid (4.3 mm). When compared to a silanized silicon surface with a departing diameter of $2.9 \pm 0.2 \text{ mm}$ (as shown in Figure 2d), a shift was also observed in the distribution of droplet diameters to smaller sizes (as shown in Figure 2e). The increased nucleation density, lower departure diameter, and droplet size distribution of the copolymer surface on a smooth silicon substrate indicate an improved condensation heat transfer coefficient according to widely-accepted models.

Dropwise Condensation Experiment B – Aluminum Substrate Experiment

[00162] Commercial condensers are typically constructed using alloys of metals such as titanium, stainless steel, copper, and aluminum. To test a prototype that was most similar to an industrial condenser, a 40 nm film of p(PFDA-co-DVB) was grafted onto 50

mm diameter aluminum substrates via iCVD. The additional roughness imparted by the metal surface ($\text{RMS} = 118 \pm 33 \text{ nm}$) was apparent in the AFM height scans (shown in Figures 3a and 3b). As expected on a rougher surface in a Wenzel state, the CAH measured during condensation at 6.9 kPa was similar ($37^\circ \pm 5^\circ$) and accordingly, the size of a departing drop ($4.2 \pm 0.1 \text{ mm}$) was larger than that on a silicon substrate (as shown in Figure 3c).

Dropwise Condensation Experiment C – Effect of Grafting

[00163] In this Example, coated substrates were tested for condensation performance in the apparatus described below and shown in Figure 6. The flow loop of the test apparatus is shown in Figure 7. Saturated steam is produced by an electric boiler using deionized feedwater with a resistivity of 5 MOhm that is further passed through a membrane vacuum degassifier to reduce dissolved oxygen to below 1 ppm. The steam is produced at 380 kPa and passes through a pressure regulator and a separator to the condensing chamber, which is evacuated before each test by a rotary vane vacuum pump. The sample is cooled by a heat exchanger operating at 60 psig with 1 MOhm deionized chilled water at 4°C.

[00164] Condensing specimens coated with p(PFDA-co-DVB) were secured in a chamber with the coated side exposed to saturated steam and the other side cooled by running water, in Figure 6. The chamber was initially evacuated to remove non-condensable vapors, and steam was introduced at a variable rate to maintain pressures ranging from 10 kPa to 100 kPa. Saturated steam was produced by an electric boiler using deionized feedwater with a resistivity of 5 MOhm that was fed through a degassifier to reduce dissolved oxygen to below 1 ppm. The rear side of the sample was

cooled by a forced chilled water at 4°C. Temperature gradients within the specimens were measured by thermistors embedded at precise locations within the specimen. The heat transfer coefficient could be determined from the temperature gradient and the surface temperature. After several hours of operation, the coated specimens exhibited an improved heat transfer coefficient.

[00165] Figures 8a-8b show (a) Grafted PFDA and (b) ungrafted PFDA samples after 1 hour of condensation in saturated steam at 90°C and 70 kPa. Figures 8c-8d also show condensate drops on (c) grafted and (d) ungrafted PFDA surfaces after 10 minutes of condensing saturated steam. The distorted drop shape on the ungrafted sample indicates severe contact line pinning following delamination of the polymer film. Departing drop sizes on ungrafted sample were 3.1 mm, compared to 2.3 mm for the grafted surface. Heat transfer coefficient was measured at 31 ± 2 kW/m²K at beginning of test, 23 ± 2 kW/m²K after deterioration of ungrafted surface. This example illustrates how covalent grafting can significantly improve the adhesion of the polymer films on metal substrates and increase their durability in the presence of condensing steam.

Dropwise Condensation Experiment D – Film Thickness & Heat Transfer Coefficient

[00166] Referring now to Figure 1a, monomer and initiator species are flowed into a reactor at controlled rates, where the monomer and initiator species encounter heated filaments and a cooled substrate, as shown in Figure 1b. The locally heated zone around the filaments thermally cleaves the initiator species (tert-butyl peroxide, TBPO). The produced radical fragments initiate vinyl polymerization of the monomers absorbed on the surface, which is held at a lower temperature. The functional groups, such as the perfluorinated side chain of PFDA, are fully preserved after polymerization.

[00167] The film thickness is measured *in-situ* during deposition, so that the process can be stopped when the thickness reaches the desired value. In some embodiments, the iCVD copolymer layers are ultra-thin (~ 40 nm), leading to an estimated contribution to total thermal resistance of less than 0.001%. To verify that the film thickness did not have an effect on the condensation heat transfer coefficient, two different thicknesses of films were measured, with the results being provided in Table 6 below. As seen in Table 6 below, the condensation heat transfer coefficients of the two film thicknesses are nearly identical.

Table 6: Effect of Film Thickness on Heat Transfer Coefficient

Thickness (nm)	h (k W m ⁻² K ⁻¹)
41.5 ± 2.4	38.1 ± 4.0
59.2 ± 6.6	39.5 ± 4.2

Dropwise Condensation Experiment E – Prolonged Exposure Experiment

[00168] Accelerated endurance tests were conducted by condensing pure saturated steam at 100°C. Coatings of p(PFDA-*co*-DVB) were compared to fluorosilane coatings, both on aluminum substrates (shown in Figures 3c and 3d). Figure 3e shows a comparison of these two surfaces, along with an uncoated aluminum surface that undergoes filmwise condensation for reference, under prolonged condensation at 103.4 kPa. Although the silanized surface initially displayed a larger heat transfer coefficient of 61 ± 2 kW m⁻² K⁻¹ due to the lower hysteresis ($31^\circ \pm 3^\circ$) and departing droplet size (3.6 ± 0.4 mm), it quickly degraded in a matter of minutes and exhibited dropwise condensation with a heat transfer coefficient of 4.6 ± 0.4 kW m⁻² K⁻¹. The grafted polymer coating exhibited dropwise condensation with a departing droplet size of 4.2 ± 0.1 mm and a heat

transfer coefficient greater than $35 \text{ kW m}^{-2} \text{ K}^{-1}$, which was more than 7 times greater than the steady-state filmwise heat transfer coefficient of the degraded silanized surface, with no noticeable degradation after 48 hours of condensation.

[00169] Grafted polymers deposited via iCVD lead to robust dropwise condensing surfaces that can sustain prolonged exposure (e.g., >48 hours) to steam at 100°C , significantly outperforming a fluorosilane treatment tested under identical conditions. A simple first-order exponential to fit to the degradation of the heat transfer coefficients results in degradation time constants of ca. 2 minutes and $O \approx 10^4$ hours for fluorosilane and grafted copolymer surfaces, respectively. Thermal degradation of films deposited using the iCVD process has previously been tested and described by a logistic model. Since degradation under a steam environment is an entirely different process, and fitting to the logistic model would require knowledge of the time required to degraded to 50%, there is a further need for longer-duration endurance tests. The unique composition of the copolymer achievable iCVD is essential for achieving low contact angle hysteresis, which results from the combination of low roughness and limited reorientation of the surface fluorinated groups between the wet and dry states. iCVD surfaces exhibit heat transfer coefficients that are more than 7 times greater than filmwise condensation when deposited on practical engineering heat transfer substrates, such as aluminum and copper. A successful industrial prototype has been demonstrated and successfully tested, indicating scalability to industrial processes.

Dropwise Condensation Experiment F – Tubing Coil Experiment

[00170] As a further demonstration of the versatility of iCVD-deposited copolymers to coat complex shapes such as heat exchanger tubing, a 40 nm thin film of p(PFDA-co-

DVB) was grafted conformally onto the outer surface of a copper tubing coil. It would have been exceedingly difficult to achieve such an ultra-thin, uniform layer by common surface modification techniques such as spray coating, spin casting and/or doctor blade application, and/or with vacuum techniques such as sputtering and/or evaporation. As shown in Figure 4, the tubing coil exhibited prolonged dropwise condensation after a single-step deposition.

Dropwise Condensation Experiment G – Hydrocarbon Condensation Experiment

[00171] To demonstrate the ability of a grafted iCVD surface to promote dropwise condensation of low-surface tension fluids, a silicon substrate coated with a thin film of p(PFDA-co-DVB) was fixed in a custom-built vacuum chamber shown in Figure 6 such that the surface was held vertically. Hydrocarbon vapors were supplied by a container filled with 30 mL of either pentane or hexane, and immersed in a water bath (Julabo FP-25) heated to 40°C. The vacuum chamber was purged three times below 0.1 kPa and above 50 kPa with pentane vapor to remove non-condensables. After purging, the rear side of the surface was cooled with forced chilled water to a temperature of around 10°C. The hydrocarbon vapor pressure was increased by opening a needle valve until the corresponding saturation temperature was greater than 10°C, thus initiating condensation of hydrocarbon vapor onto the chilled copolymer surface. Figure 20a and 20b show snapshots of dropwise condensation of hexane on a copolymer film. Hexane CAH and departing diameter are also shown in Figure 20b. Heat transfer coefficients during condensation of pentane vapor were measured by thermistors embedded behind the surface. The condensation heat transfer coefficient of pentane was 22.5 kW/m²K,

condensing at a pressure of 52.0 kPa saturation temperature 17.7°C, surface temperature 17.4°C, and a heat flux of 7.3 kW/m².

Equivalents

[00172] While the invention has been particularly shown and described with reference to specific preferred embodiments, it should be understood by those skilled in the art that various changes in form and detail may be made therein without departing from the spirit and scope of the invention as defined by the appended claims.

[00173] What is claimed is:

1. An article for enhanced heat transfer, and/or mitigating phase transition and nucleation of undesired materials, and/or reducing adhesion of liquids and solids thereupon, the article comprising a substrate and a (e.g., thin, uniform) polymeric film grafted (e.g., covalently bonded) thereupon.
2. The article of claim 1, wherein the substrate comprises a metal (e.g., steel, stainless steel, titanium, nickel, copper, aluminum, molybdenum, and/or alloys thereof).
3. The article of claim 1, wherein the substrate comprises a polymer (e.g., polyethylene, polyvinylchloride, polymethylmethacrylate, polyvinylidene fluoride, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, polyisoprene, synthetic rubber, polytetrafluoroethylene, polyethylene terephthalate, acrylate polymer, chlorinated rubber, fluoropolymer, polyamide resin, vinyl resin, expanded polytetrafluoroethylene, low density polyethylene, high density polyethylene, and/or polypropylene).
4. The article of claim 1, wherein the substrate comprises a semiconductor and/or ceramic (e.g., SiC, Si, AlN, GaAs, GaN, ZnO, Ge, SiGe, BN, BAs, AlGaAs, TiO₂, TiN, etc.).
5. The article of claim 1, wherein the substrate comprises a rare earth element or compound comprising a rare earth element (e.g., a rare earth oxide, carbide, nitride, fluoride, or boride; e.g., cerium oxide CeO₂).

6. The article of any one of claims 1-5, wherein the polymeric film comprises a fluoropolymer.
7. The article of any one of the preceding claims, wherein the polymeric film is formed from at least one monomer species comprising one or more pendant perfluorinated alkyl moieties.
8. The article of claim 6, wherein the fluoropolymer has at least one CF₃ group.
9. The article of claim 6, wherein the fluoropolymer comprises polytetrafluoroethylene (PTFE).
10. The article of claim 6, wherein the fluoropolymer comprises [C₁₂H₉F₁₃O₂]_n, where n is an integer greater than zero.
11. The article of claim 6, wherein the fluoropolymer comprises a member selected from the group consisting of poly(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate), poly(1H, 1H, 2H, 2H - perfluorooctyl acrylate), poly([N-methyl-perfluorohexane-1-sulfonamide] ethyl acrylate), poly([N-methyl-perfluorohexane-1-sulfonamide] ethyl (meth) acrylate), poly(2-(Perfluoro-3-methylbutyl)ethyl methacrylate)), poly(2-[[[2- (perfluorohexyl)ethyl]sulfonyl]methyl]-amino]ethyl]acrylate), poly(2-[[[2- (perfluoroheptyl)ethyl]sulfonyl]methyl]-

amino]ethyl]acrylate), poly(2-[[[2- (perfluorooctyl)ethyl]sulfonyl]methyl]-amino]ethyl]acrylate), and any copolymer thereof.

12. The article of claim 6, wherein the fluoropolymer is a C6 analog of PFDA.

13. The article of claim 6, wherein the fluoropolymer comprises poly(2-(Perfluoro-3-methylbutyl)ethyl methacrylate), or any copolymer comprising 2-(Perfluoro-3-methylbutyl)ethyl methacrylate, wherein the fluoropolymer is crosslinked.

14. The article of any one of the preceding claims, wherein the polymeric film comprises at least one member selected from the group consisting of polytetrafluoroethylene (PTFE), poly(perfluorodecylacrylate) (PFDA), polymethylmethacrylate (PMMA), polyglycidylmethacrylate (PGMA), poly-2-hydroxyethylmethacrylate, poly(perfluorononyl acrylate), poly(perfluorooctyl acrylate), and any copolymer thereof.

15. The article of any one of the preceding claims, wherein the polymeric film comprises a copolymer of two or more monomer species.

16. The article of any one of the preceding claims, wherein the polymeric film comprises cross-linked polymer and/or cross-linked copolymer.

17. The article of claim 16, where the polymeric film is cross-linked with a crosslinking agent comprising an organic molecule having at least two vinyl moieties.
18. The article of claim 16, where the polymeric film is cross-linked with a crosslinking agent comprising at least one member selected from the group consisting of: diethyleneglycol divinyl ether, diethyleneglycol dimethacrylate, diethyleneglycol diacrylate, and/or 1H,1H,6H,6H-perfluorohexyldiacrylate.
19. The article of claim 16, where the polymeric film is cross-linked with divinyl benzene (DVB).
20. The article of claim 16, wherein the polymeric film is cross-linked with a member selected from the group consisting of ethylene dimethacrylate (EDMA), di(ethyleneglycol)di(methacrylate), di(ethyleneglycol)di(acrylate), ethyleneglycoldimethacrylate (EGDMA), di(ethyleneglycol)di(vinylether) (EDGDVE), and 1H,1H,6H,6H-perfluorohexyldiacrylate.
21. The article of any one of claims 16 to 20, wherein the polymeric film comprises from 0 wt. % to 99 wt.% crosslinking agent (e.g., from 5 wt.% to 90 wt.%; from 15 wt.% to 85 wt.%; from 25 wt.% to 75 wt.%; from 35 wt.% to 65 wt.%; or from 45 wt.% to 55 wt.%).

22. The article of any one of claims 16 to 21, wherein the polymeric film has non-uniform concentration of crosslinking agent along the thickness of the film.
23. The article of any one of the preceding claims, wherein the polymeric film is covalently bonded to the substrate.
24. The article of any one of the preceding claims, wherein the polymeric film is covalently bonded to the substrate by attachment of a vinyl precursor to the substrate, thereby forming a surface comprising a plurality of pendant vinyl moieties.
25. The article of claim 24, wherein the vinyl precursor is a member selected from the group consisting of a vinyl functional silane, a vinyl functional phosphonic acid, and a vinyl functional thiol.
26. The article of claim 24 or 25, wherein the vinyl precursor comprises at least one member selected from the group consisting of trichlorovinylsilane, bis(triethoxysilyl)ethylvinylmethy- silane, bis(triethoxysilyl)ethylene, bis(trimethoxysilyl)ethylmethy- lene, 1,3-[bis(3-triethoxysilylpropyl)poly- ethylenoxy]-2-methylenepropane, bis[(3-trimethoxysilyl)propyl]-ethylenediamine, bis[3-(triethoxysilyl)propyl]- disulfide, 3-mercaptopropyltrimethoxysilane, and vinyl phosphonic acid.

27. The article of any one of the preceding claims, wherein the polymeric film is no greater than 500 nm in thickness (e.g., no greater than 400 nm, no greater than 300 nm, no greater than 200 nm, no greater than 100 nm, no greater than 75 nm, no greater than 50 nm, no greater than 25 nm, or no greater than 15 nm, e.g., as thin as 10 nm).

28. The article of claim 27, wherein the polymeric film comprises a grafting layer (e.g., where the polymeric film is covalently bonded to the substrate) and a bulk film layer (e.g., where the grafting layer has a thickness from about 0.5 nm to about 5 nm, or from about 1 nm to about 3 nm, or from about 1 nm to about 2 nm).

29. The article of any one of the preceding claims, wherein the polymer film has a thickness variation of no greater than about 20% (e.g., no greater than about 15%, no greater than about 10%, or no greater than about 5% -- e.g., the polymer film is uniform).

30. The article of any one of the preceding claims, wherein the polymer film has a texture comprising micro- and/or nano-scale features (e.g., ridges, grooves, pores, posts, bumps, and/or protrusions, patterned and/or unpatterned).

31. The article of any one of the preceding claims, wherein the substrate is textured and wherein the polymeric film conforms to the textured substrate surface.

32. The article of claim 31, wherein the substrate is textured with micro- and/or nano-scale surface textures (e.g., posts, ridges, cavities, pores, posts, protrusions, etc.).

33. The article of any one of the preceding claims, wherein the polymeric film has a crystalline or semicrystalline surface (e.g., formed via annealing, but not necessarily via annealing).

34. The article of any one of the preceding claims, wherein the polymeric film has a surface (e.g., exposed surface) with low contact angle hysteresis (e.g., no greater than 50°, no greater than 40°, no greater than 30°, no greater than 25°, no greater than 20°, no greater than 15°, or no greater than 10°, or no greater than 5°, or no greater than 1° for water; and no greater than 20°, no greater than 15°, no greater than 10°, no greater than 5°, or no greater than 1° for hydrocarbons, refrigerants, cryogenic liquids, and other low-surface tension liquids, where contact angle hysteresis is the difference between advancing contact angle and receding contact angle).

35. The article of any one of the preceding claims, wherein the polymeric film has a surface (e.g., exposed surface) with high advancing contact angle (e.g., no less than 70°, no less than 80°, no less than 90°, no less than 100°, no less than 120°, no less than 130°, no less than 140° for water; and no less than 30°, no less than 40°, no less than 50°, no less than 60°, no less than 70°, no less than 80°, no less than 90°, no less than 100° for hydrocarbons, refrigerants, cryogenic liquids, and other low-surface tension liquids) and/or high receding contact angle (e.g., no less than 60°, no less than 70°, no less than 80°, no less than 90°, no less than 100°, no less than 110°, or no less than 120° for water; and no less than 20°, no less than 30°, no less than 40°, no less than 50°, no less than 60°,

no less than 70°, no less than 80°, no less than 90° for hydrocarbons, refrigerants, cryogenic liquids, and other low-surface tension liquids).

36. The article of any one of the preceding claims, wherein the article is a condenser (e.g., where dropwise condensation is promoted on the surface of the polymeric film for enhanced heat transfer).

37. The article of any one of the preceding claims, wherein the article is a cooling device for an electronic and/or photonic component (e.g., where heat transfer is promoted from the electronic or photonic component to the surface of the polymeric film, wherein the polymeric film is in contact with the component, and/or wherein the polymeric is in contact with a fluid that is in contact with the component).

38. The article of any one of the preceding claims, wherein the article is flexible.

39. The article of any one of the preceding claims, wherein the substrate and the polymeric film grafted thereupon is flexible.

40. The article of any one of the preceding claims, wherein the article is retrofitted to form the grafted polymeric film.

41. The article of any one of the preceding claims, wherein the polymeric film comprises a polymer and/or copolymer, the polymer and/or copolymer comprising at

least one perfluorinated pendant chain (e.g., a perfluorinated acrylate and/or a perfluorinated cyclic group, e.g., with 4 to 6 carbons in the ring), a spacer group, and a vinyl-based backbone group.

42. A method of using an article of any one of the preceding claims, wherein the method comprises contacting an exposed surface of the polymeric film with a Thermal Interface Material (TIM) (e.g., a thermally conductive material used between microprocessors and heatsinks to increase thermal transfer efficiency).

43. A method of preparing an article of any one of claims 1-41, the method comprising the step of performing hot wire CVD (HWCVD) to produce the polymeric film grafted on the substrate.

44. The method of claim 43, wherein the step of performing HWCVD comprises performing initiated chemical vapor deposition (iCVD) to produce the polymeric film grafted on the substrate.

45. The method of claim 43 or 44, further comprising the step of annealing the polymeric film by exposure to heat (e.g., to increase crosslinking density and/or degree of crystallinity of the polymeric film).

46. The method of any one of claims 43 to 45, wherein the HWCVD step is performed to retrofit an existing article (e.g., a condenser, boiler or other heat transfer

surface in an HVAC device, a power plant, a desalination plant, a natural gas liquefaction ship, etc.) by grafting the polymeric film upon a surface thereof.

47. The article of any one of claims 1 to 41, wherein the article is a Thermal Interface Material (TIM).

48. The article of any one of claims 1 to 41, wherein the polymeric film has an exposed surface with critical surface energy no greater than 18 mN/m.

49. The article of claim 48, wherein the polymeric film has an exposed surface with critical surface energy no greater than 6 mN/m.

50. The article of any one of claims 1-41 or 47-49, wherein the polymeric film has an exposed surface with contact angle hysteresis no greater than 25° for water, hydrocarbons, refrigerants, cryogenic liquids, and other heat transfer fluids.

51. The article of claim 50, wherein the exposed surface has contact angle hysteresis no greater than 1° or no greater than 5° for water, hydrocarbons, refrigerants, cryogenic liquids, and other heat transfer fluids.

52. The article of any one of claims 1-41 or 47-51, wherein the polymeric film has RMS roughness no greater than 100 nm (e.g., no greater than 100 nm, no greater than 75 nm, no greater than 50 nm).

53. The article of any one of claims 1-41 or 47-52, wherein the polymeric film provides dropwise condensation and shedding of a hydrocarbon, refrigerant, cryogenic liquid, water, or other low-surface tension liquid.

54. The article of claim 53, wherein the hydrocarbon liquid is a member selected from the group consisting of alkanes, alkenes, alkynes, and fuel mixtures (e.g., gasoline, kerosene, diesel, fuel oil); the refrigerant is a member selected from the group consisting of chlorofluorocarbons, hydrofluorocarbons, and hydrochlorofluorocarbons; and the cryogenic liquid is selected from the group consisting of N₂, O₂, CO₂, He, LNG, methane, butane, propane, and isobutene.

55. The article of claim 53 or 54, wherein the hydrocarbon liquid has surface tension no greater than 30 mN/m (e.g., no greater than 28 mN/m, no greater than 21 mN/m, no greater than 18 mN/m, no greater than 16 mN/m, or no greater than 12 mN/m, or no greater than 6 mN/m).

56. The article of any one of claims 1-41 or 47-55, wherein the article is a component (e.g., vessel, pipe, fin, etc.) of a condenser that comes into contact with a condensing liquid (e.g., working fluid).

57. The article of any one of claims 1-41 or 47-56, wherein the article is a component of an oil and/or gas processing apparatus (e.g. fractionation column, liquefaction device).

58. The article of any one of claims 1-41 or 47-57, wherein the article is (or is a component of) a power line, a turbine, an aircraft, a pipeline, a boiler, a windshield, a solar panel, industrial machinery, cookware, a consumer electronic device, a printed circuit board, an electronic component, or a medical device.

59. A method for manufacturing a surface for promoting dropwise condensation and/or shedding of a liquid, the method comprising the steps of:

providing a substrate; and

controllably depositing a polymeric film on the substrate via initiated chemical vapor deposition (iCVD).

60. The method of claim 59, wherein the method comprises depositing a vinyl precursor on the substrate prior to, or concurrently with, depositing the polymeric film.

61. The method of claim 59, wherein the method comprises modulating an average roughness of the deposited layer (e.g., such that roughness is no greater than 100 nm, or no greater than 75 nm, or no greater than 50 nm).

62. The method of claim 61, wherein the modulating comprises monitoring a degree of crystallization of the deposited polymeric film; or controlling the proportion of crosslinker; or controlling a temperature of the substrate during deposition; or any combination thereof.

63. The method of any one of claims 59-62, wherein the deposited polymeric film has an average thickness from 1 nm to 1 micron.

64. The method of claim 63, wherein the deposited polymeric film has an average thickness from 1 nm to 100 nm.

65. The method of any one of claims 59-64, wherein the substrate comprises one or more materials selected from the group consisting of a metal (e.g., copper, brass, stainless steel, aluminum, aluminum bronze, nickel, iron, nickel iron aluminum bronze, titanium, scandium, and any alloys thereof), polymer, glass, rubber, silicon, polycarbonate, PVC, ceramic, semiconductor, and any combinations thereof.

66. The method of any one of claims 59-64, wherein the substrate comprises one or more materials selected from the group consisting of plastic, silicon, quartz, woven or non-woven fabric, paper, ceramic, nylon, carbon, polyester, polyurethane, polyanhydride, polyorthoester, polyacrylonitrile, polyphenazine, polyisoprene, synthetic rubber, polytetrafluoroethylene, polyethylene terephthalate, acrylate polymer, chlorinated rubber, fluoropolymer, polyamide resin, vinyl resin, expanded polytetrafluoroethylene, low density polyethylene, high density polyethylene, and polypropylene.

67. The method of any one of claims 59-66, wherein the polymeric film has an exposed surface with critical surface energy no greater than 18 mN/m.

68. The method of any one of claims 59-67, wherein the polymeric film has an exposed surface with critical surface energy no greater than 6 mN/m.
69. The method of any one of claims 59-68, wherein the polymeric film has an exposed surface with contact angle hysteresis no greater than 25°.
70. The method of claim 69, wherein the exposed surface has contact angle hysteresis no greater than 5° for water, hydrocarbons, refrigerants, cryogenic liquids, and other heat transfer fluids, or any combination thereof.
71. The method of any one of claims 59-70, wherein the polymeric film has roughness no greater than 100 nm (e.g., no greater than 100 nm, no greater than 75 nm, no greater than 50 nm).
72. The method of any one of claims 59-71, wherein the polymeric film provides dropwise condensation and shedding of a hydrocarbon, refrigerant, cryogenic liquid, water, other low-surface tension liquids, or any combination thereof.
73. The method of claim 72, wherein the hydrocarbon liquid is a member selected from the group consisting of alkanes, alkenes, alkynes, and fuel mixtures (e.g., gasoline, kerosene, diesel, fuel oil); the refrigerant is a member selected from the group of chlorofluorocarbons, hydrofluorocarbons, and hydrochlorofluorocarbons; and the

cryogenic liquid is selected from the group consisting of N₂, O₂, CO₂, LNG, methane, propane, isobutene, and any combination thereof.

74. The method of claim 73, wherein the hydrocarbon liquid has surface tension no greater than 30 mN/m (e.g., no greater than 28 mN/m, no greater than 21 mN/m, no greater than 18 mN/m, no greater than 16 mN/m, or no greater than 12 mN/m, or no greater than 6 mN/m).

75. A method for manufacturing the polymeric film on the article of any one of claims 1-41 or 47-58.

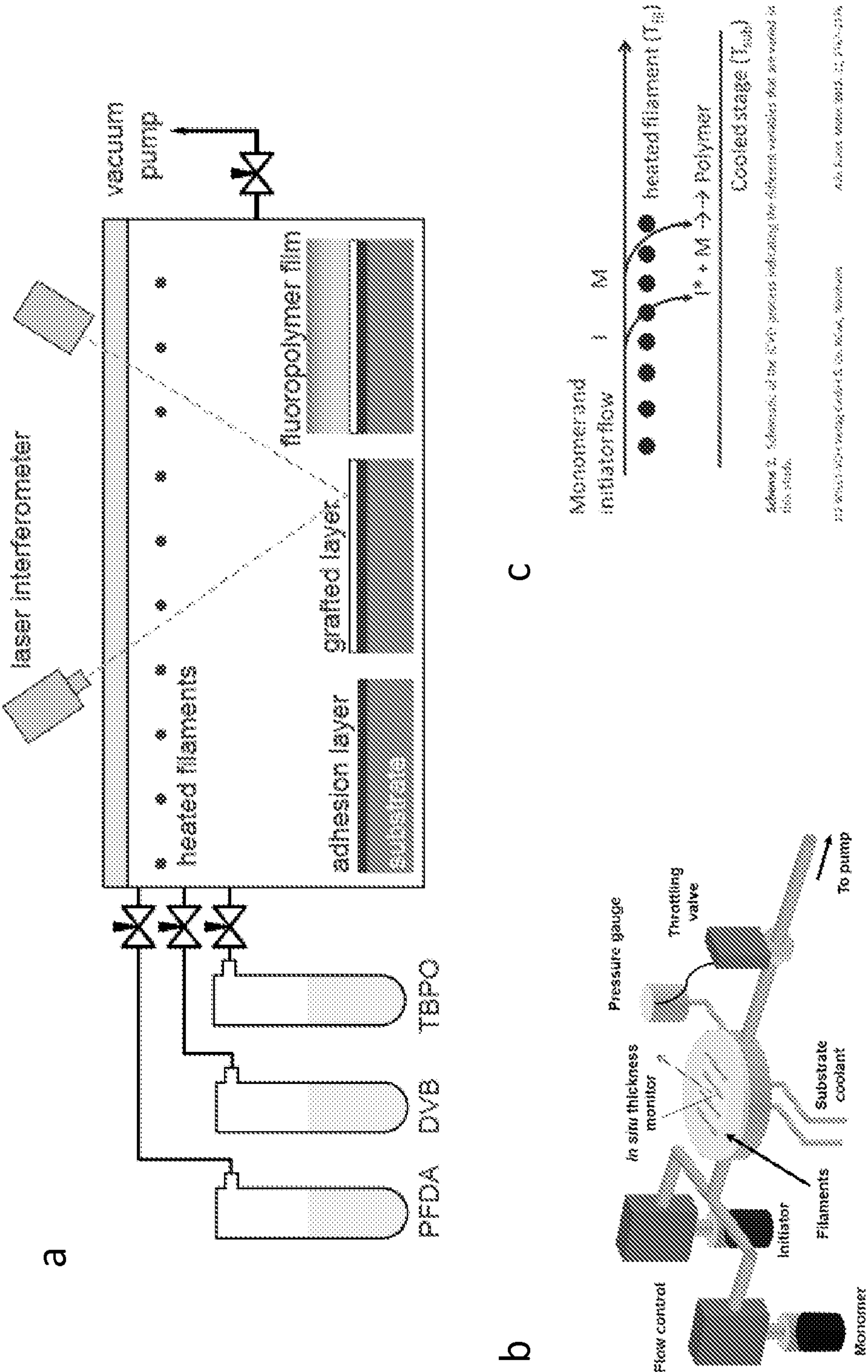


FIG. 1

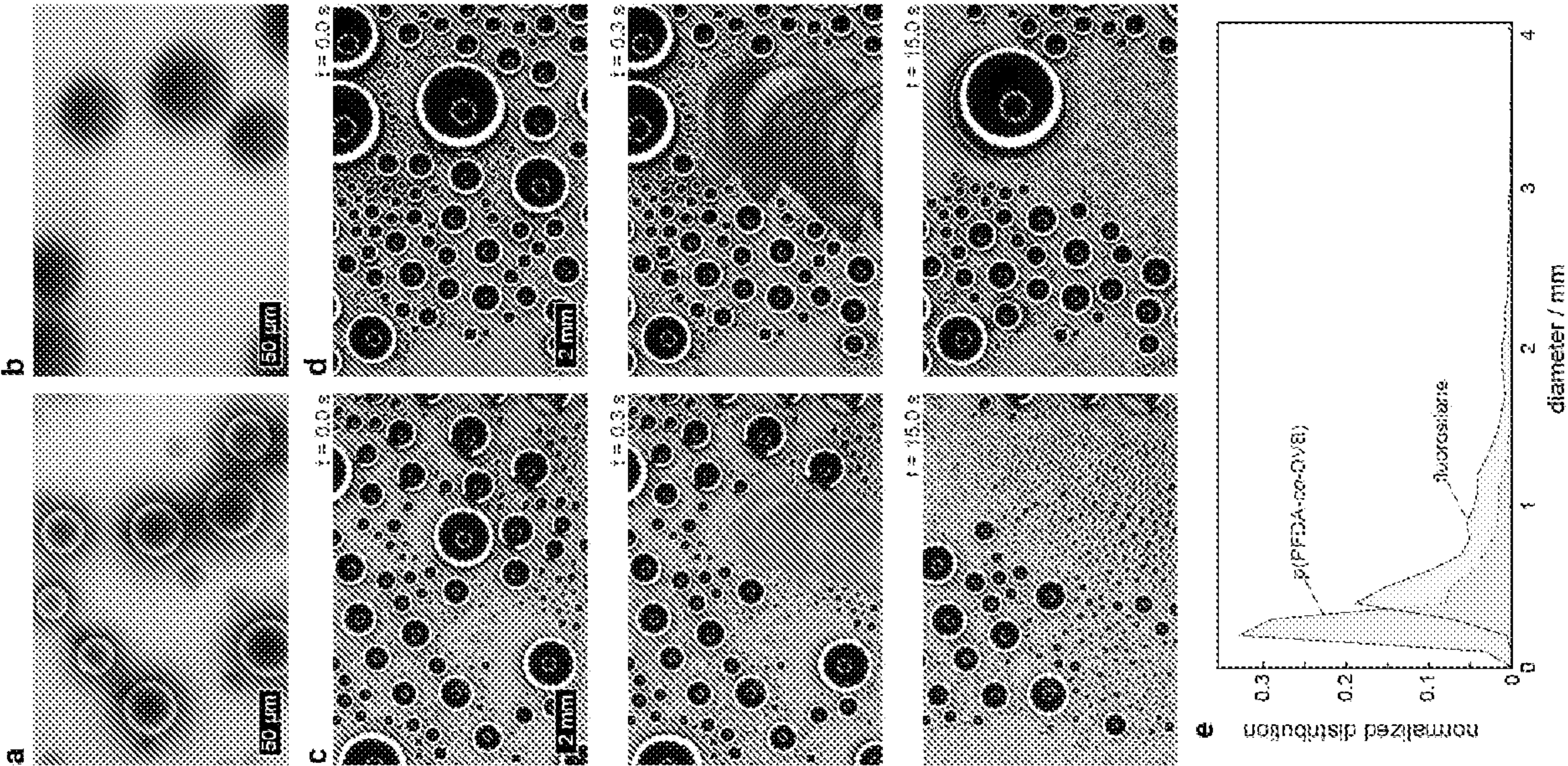


FIG. 2

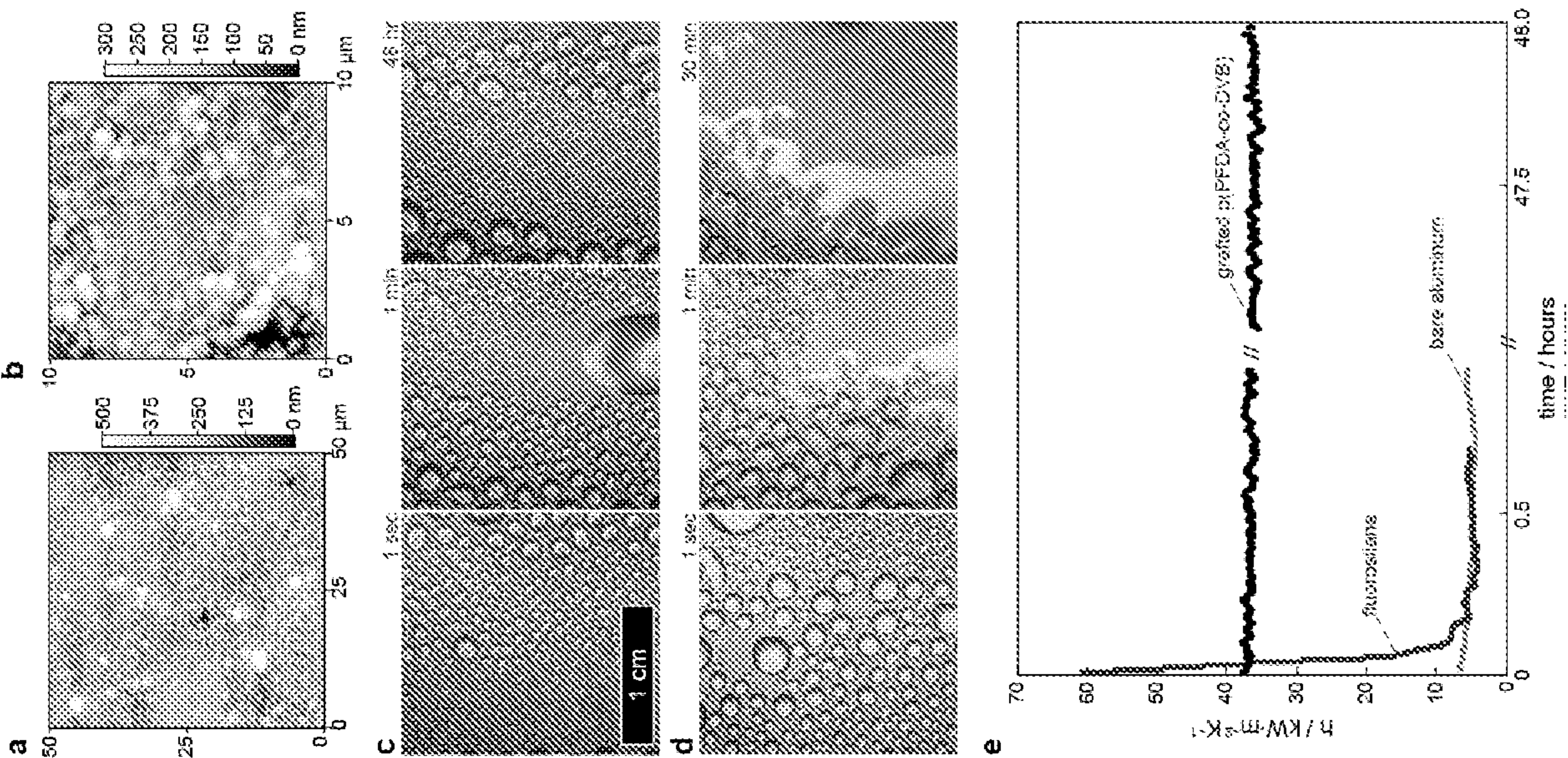


FIG. 3

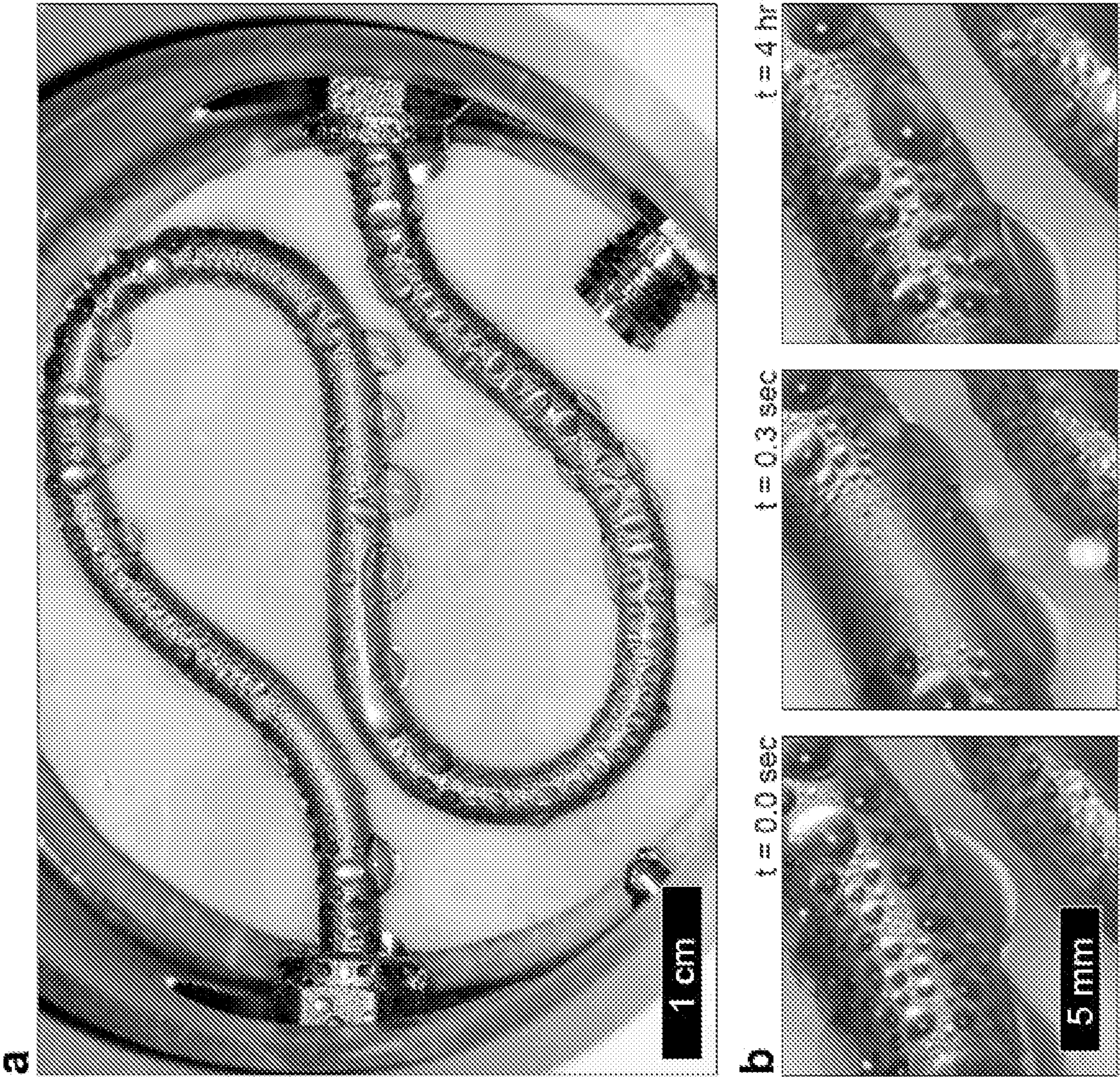


FIG. 4

5/24

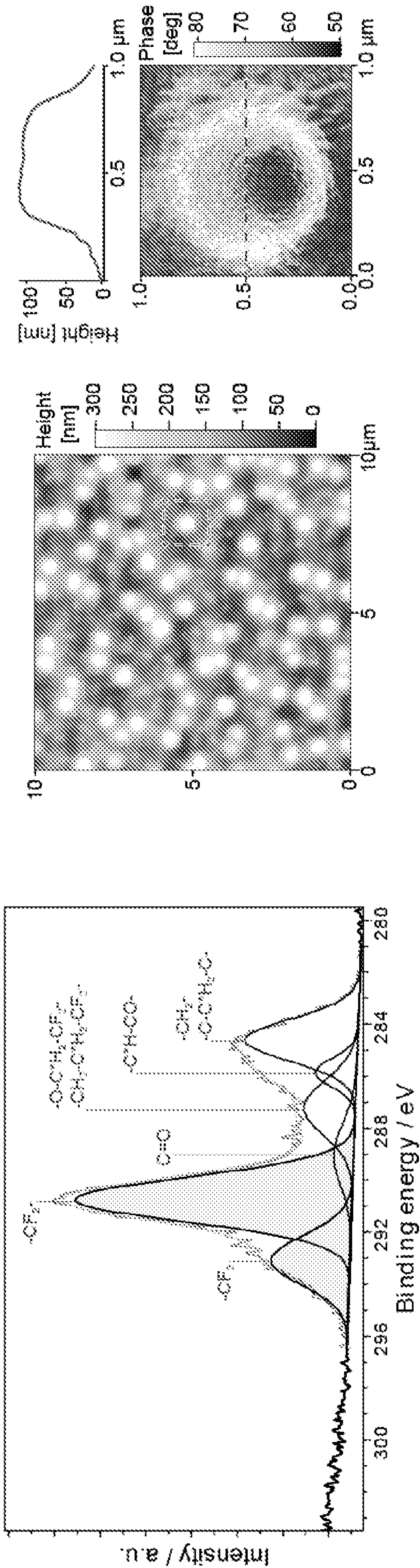


FIG. 5

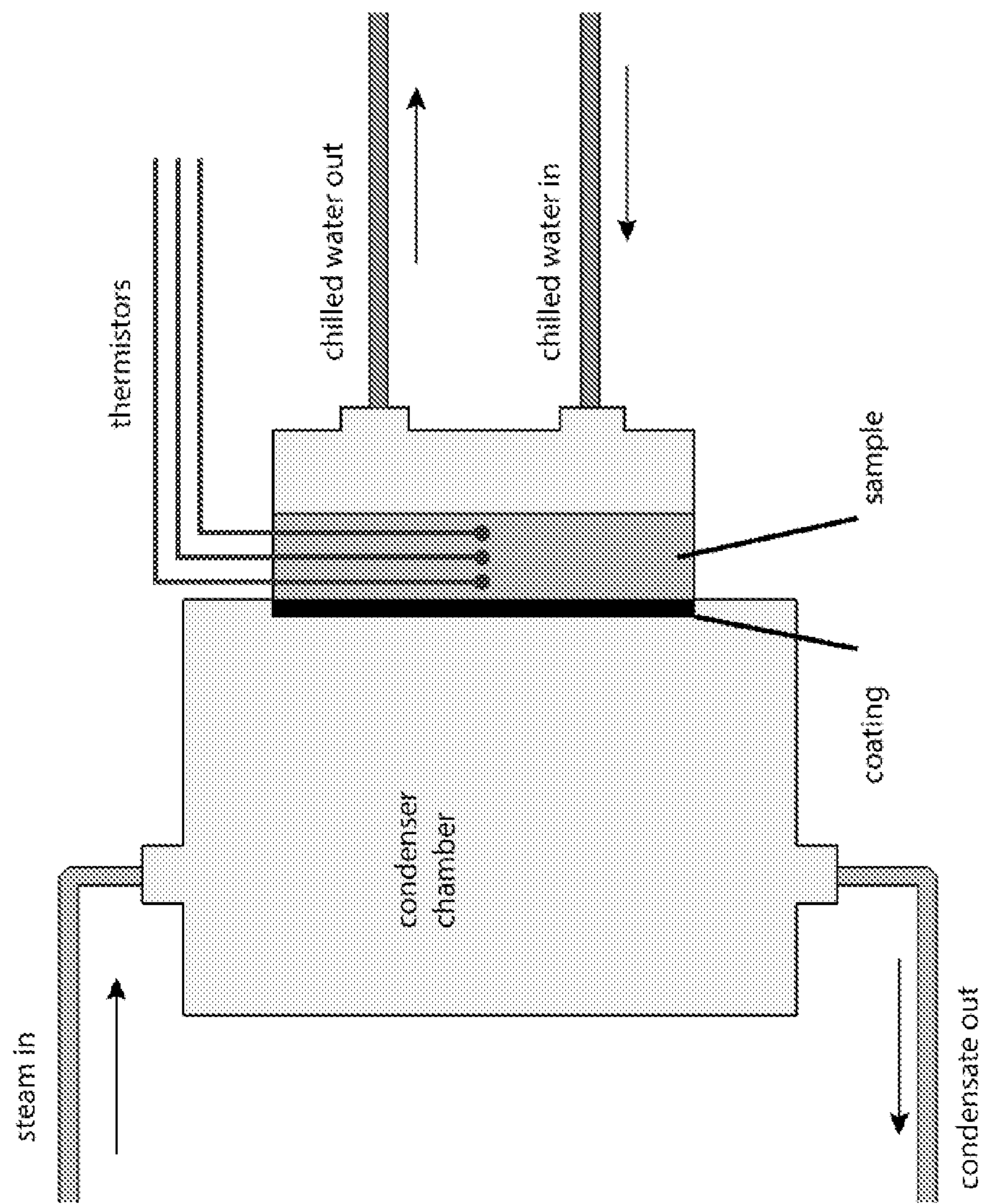


FIG. 6

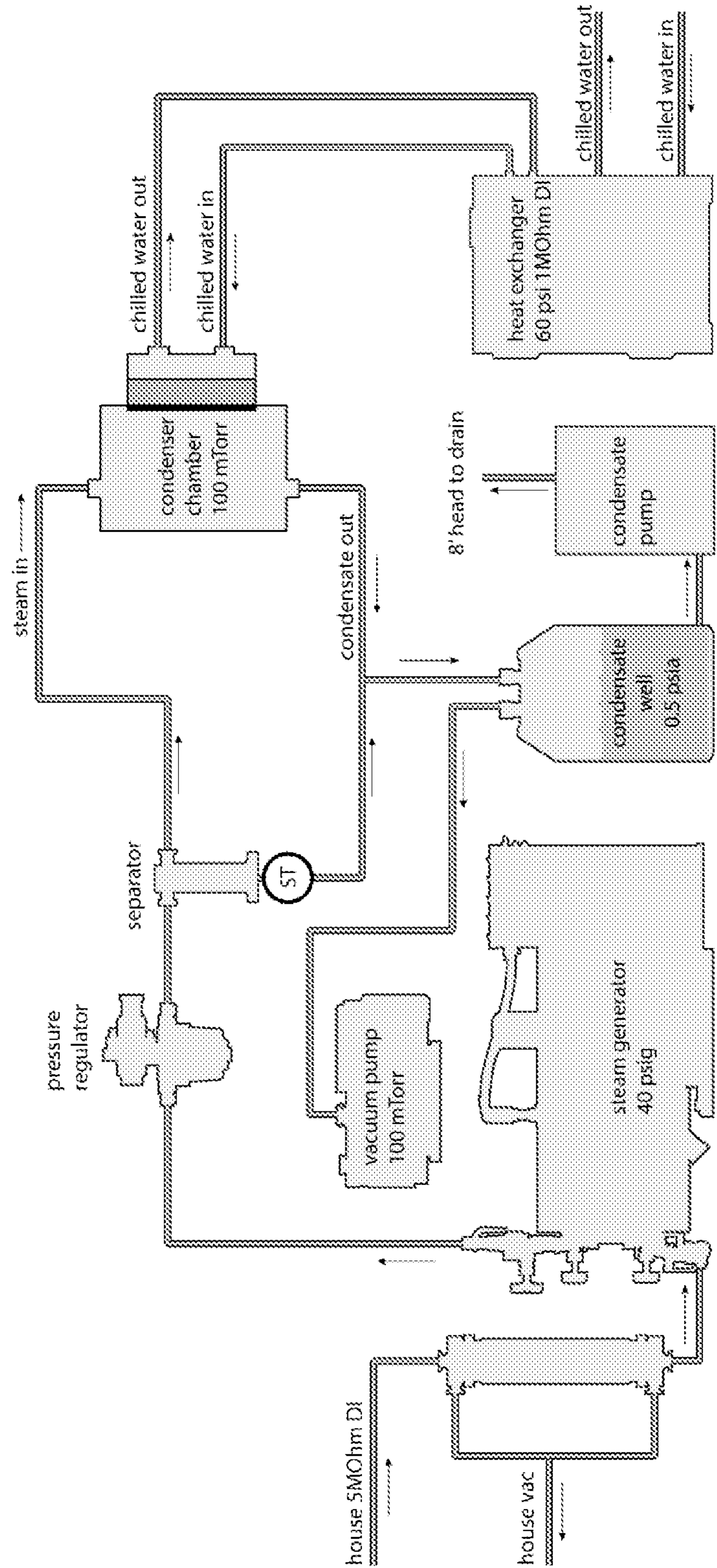


FIG. 7

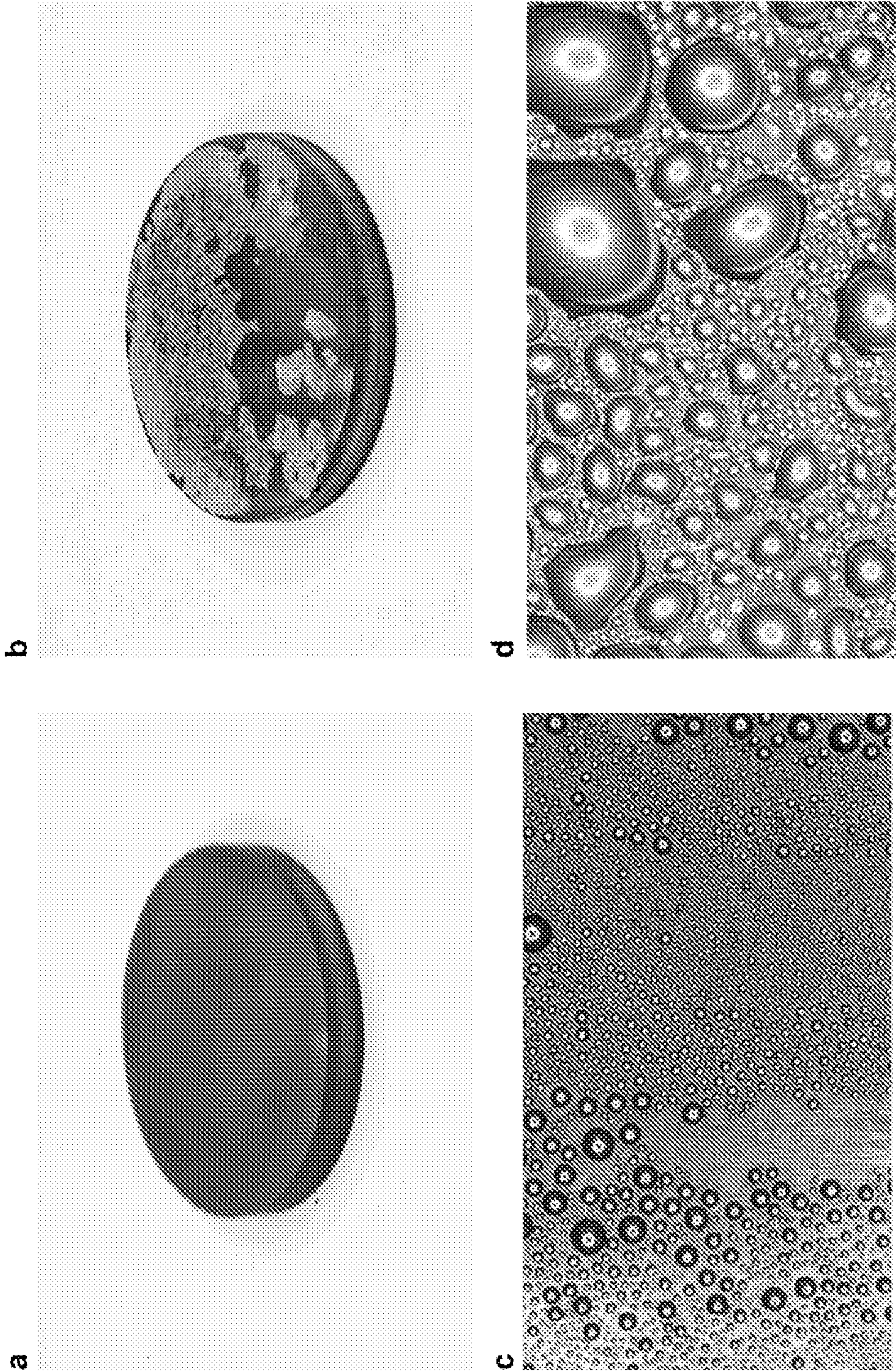


FIG. 8

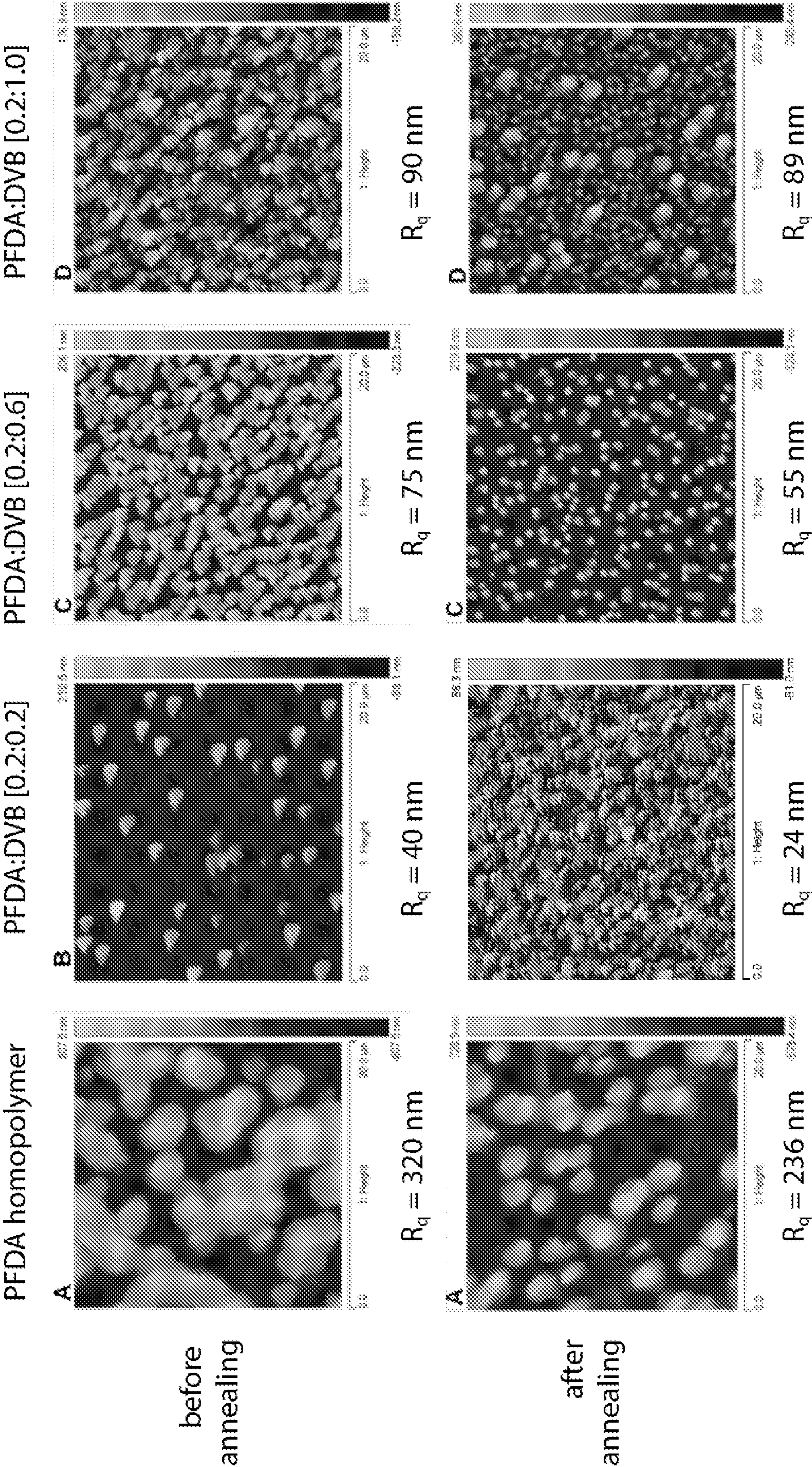


FIG. 9

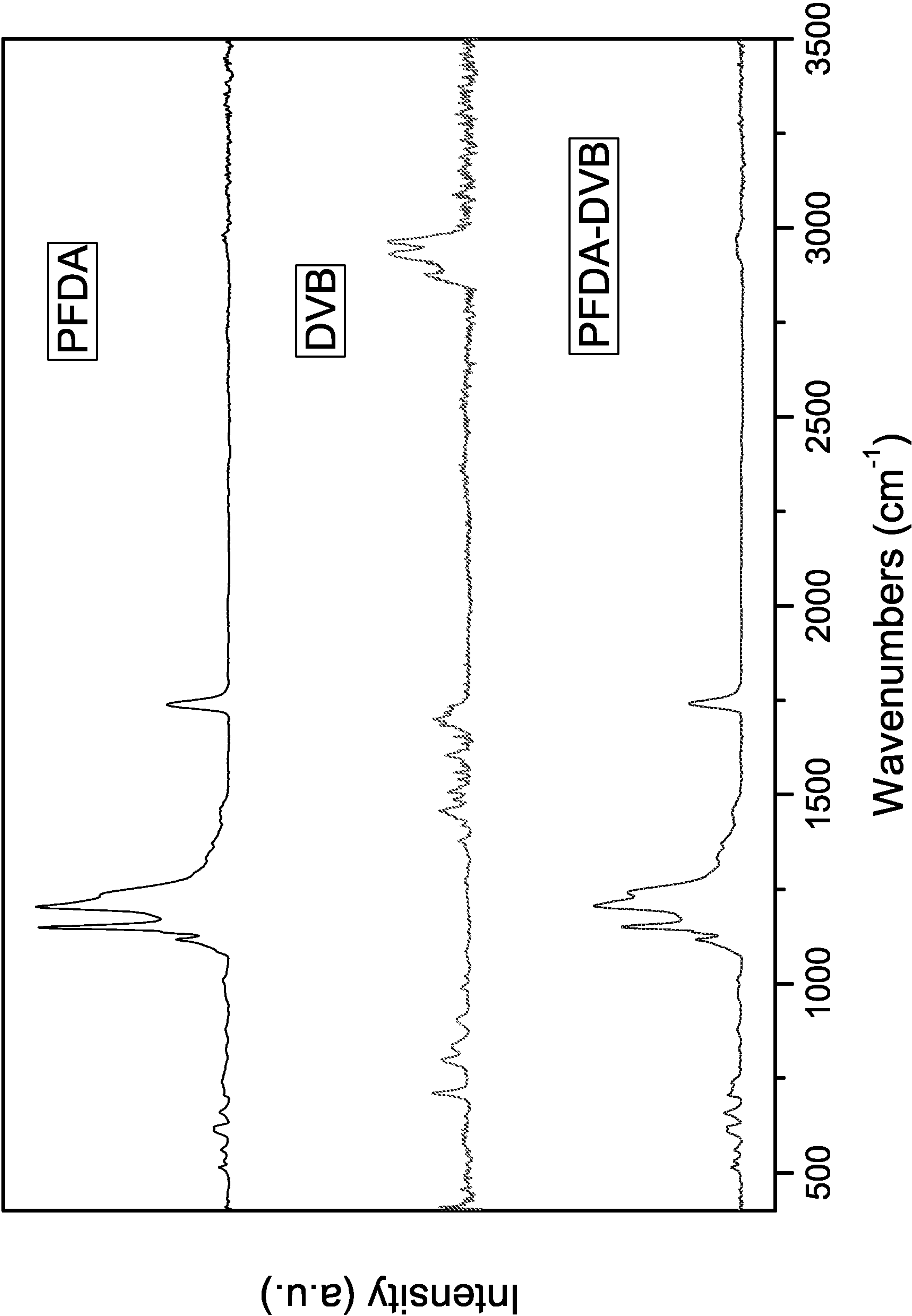


FIG. 10

Contact Angle

Water Mineral oil	PFDA thermal			
	Advancing	Receding	Hysteresis	
	140±2.1	111±1.0	29±2.0	
	90±2.3	66±4.9	24±4.3	

Water Mineral oil	PFDA-DVB_2_thermal			
	Advancing	Receding	Hysteresis	
	139±1.3	129±1.2	10±1.9	
	91±1.3	82±1.9	8±2.8	

Water Mineral oil	PFDA-DVB_3_thermal			
	Advancing	Receding	Hysteresis	
	132±1	127±1.2	5±0.9	
	85±0.2	85±0.5	0.3±0.2	

Water Mineral oil	PFDA-DVB_4_thermal			
	Advancing	Receding	Hysteresis	
	124±0.5	118±1.5	6±1.4	
	84±0.4	83±0.5	1±0.2	

Water Mineral oil	PFDA-DVB_1_13/03/12_thermal			
	Advancing	Receding	Hysteresis	
	122±0.6	116±1.7	6±1.4	
	93±0.6	79±0.7	14±1.2	

Water Mineral oil	PFDA (°)			
	Advancing	Receding	Hysteresis	
	140±0.2	117±1.8	24±1.9	
	91±0.15	64±1.4	26±1.5	

Water Mineral oil	PFDA-DVB_2 (0.2-1)			
	Advancing	Receding	Hysteresis	
	146±2.2	129±1.7	16±3.2	
	94±0.7	69±0.6	25±1.1	

Water Mineral oil	PFDA-DVB_3 (0.2-0.6)			
	Advancing	Receding	Hysteresis	
	140±5.8	125±3.4	16±3.3	
	96±0.6	64±0.7	32±1.3	

Water Mineral oil	PFDA-DVB_4 (0.2-0.2)			
	Advancing	Receding	Hysteresis	
	135±0.9	117±3.1	18±3.6	
	90±0.05	73±0	17±0.05	

Water Mineral oil	PFDA-DVB_1 (0.1-0.1)_13/03/12			
	Advancing	Receding	Hysteresis	
	142±3.2	115±1.5	28±2.9	
	98±0.3	60±0.9	38±0.7	

Water Mineral oil	DVB			
	Advancing	Receding	Hysteresis	
	93±0.5	58±0.5	34,7±0	
	28±1.8	19±2.2	9±3.4	

FIG. 11

Water Contact Angle

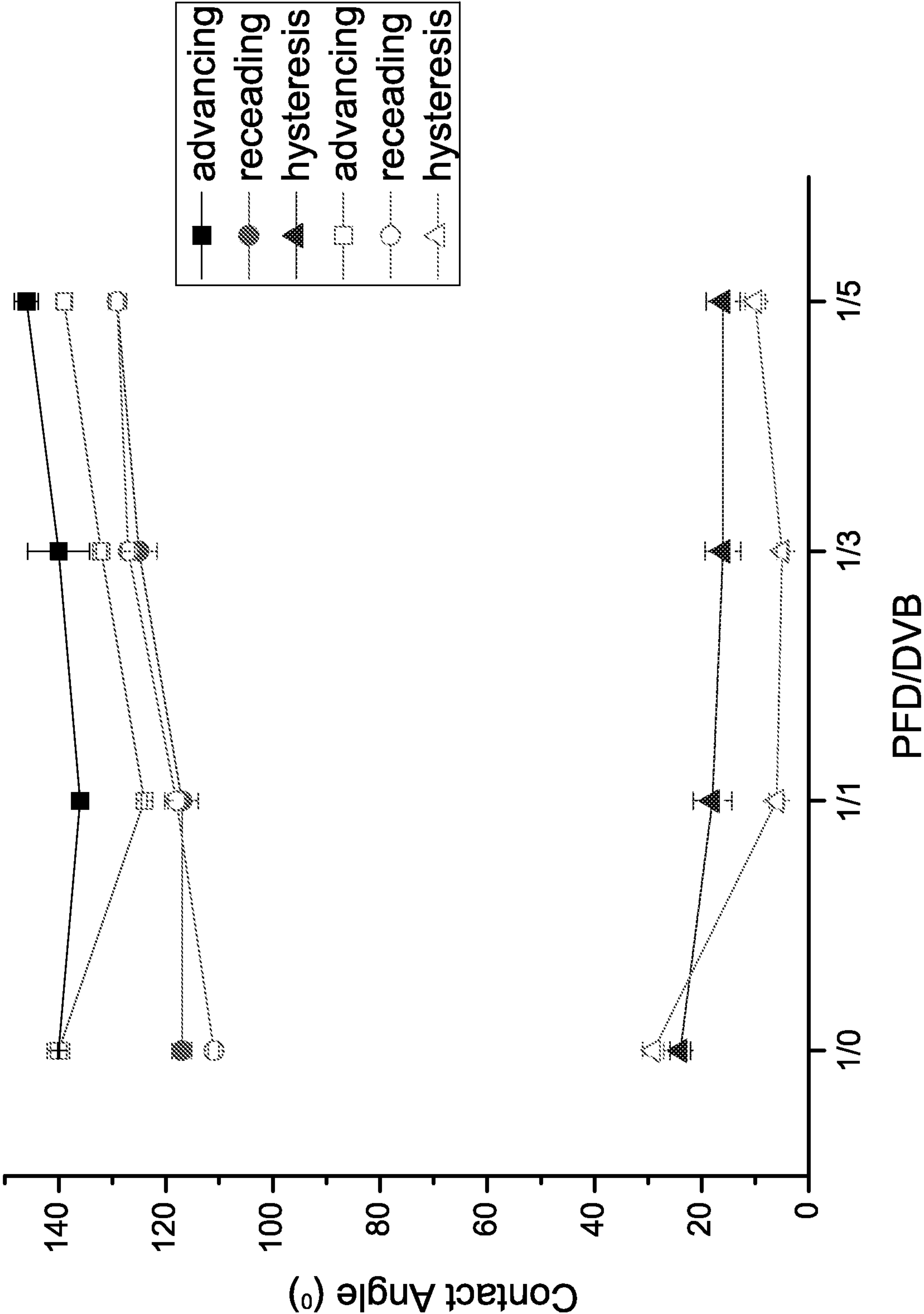


FIG. 12

Mineral Oil Contact Angle

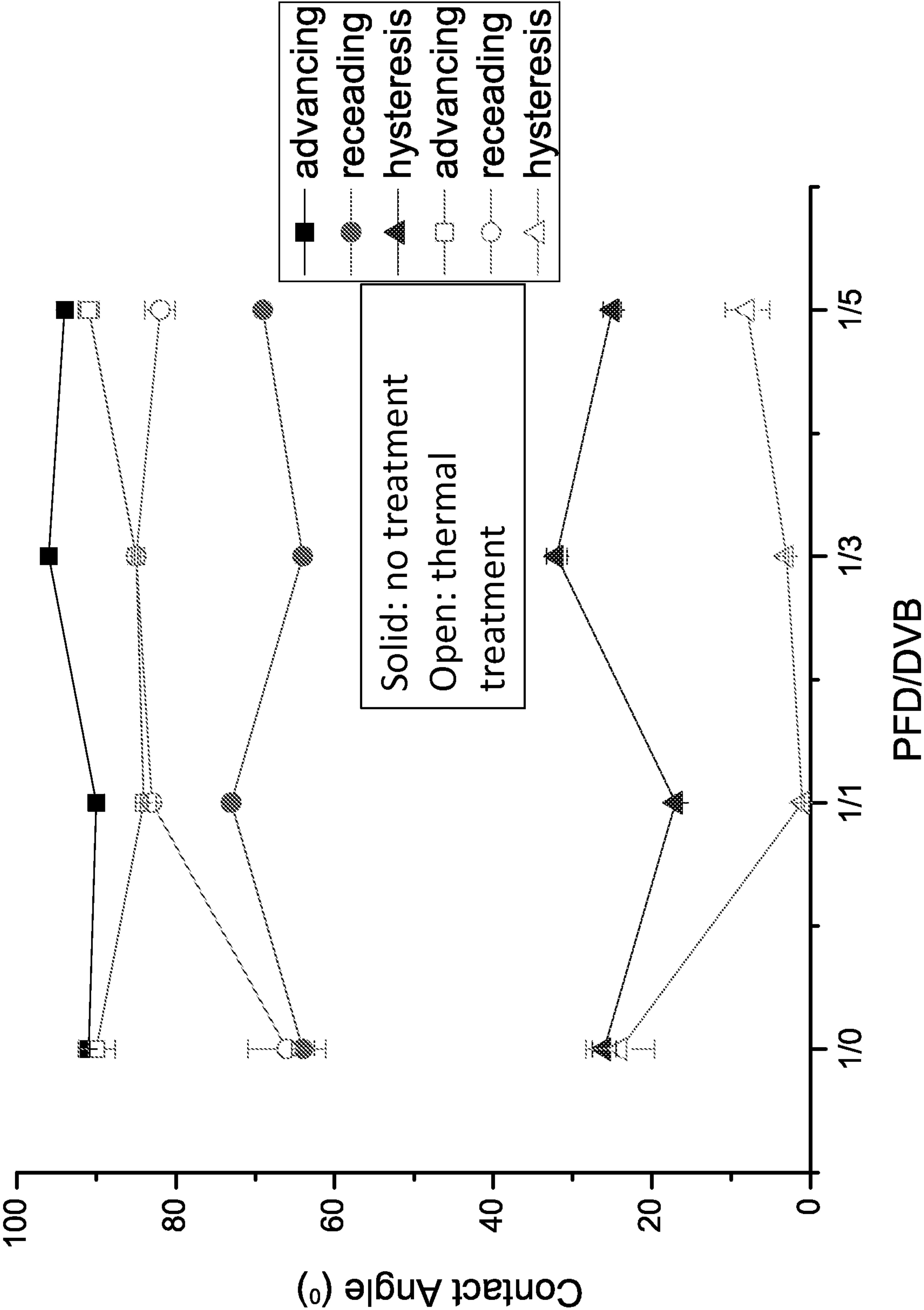
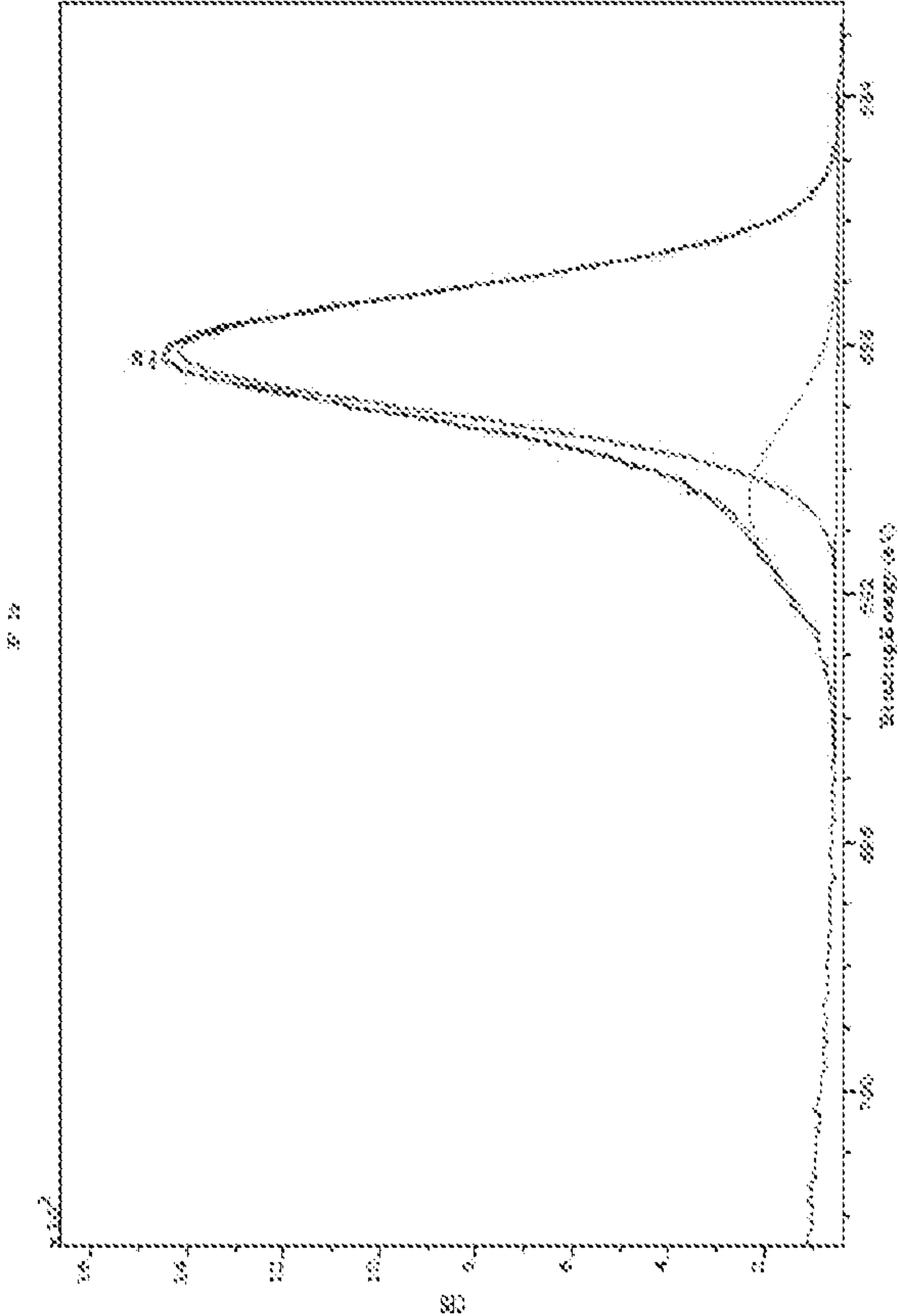


FIG. 13

XPS (0 take-off)



4. 140312 PFDA-DVB_1	0,2	1
B.E. (eV)	688,1	691,7
%	71,2	28,8

13. 140312 PFDA-DVB_4	0,2	0,2
B.E. (eV)	688,1	690
%	88,17	11,83

11. 140312 PFDA-DVB_3	0,2	0,6
B.E. (eV)	688,1	690,5
%	85,28	14,72

FIG. 14

XRD

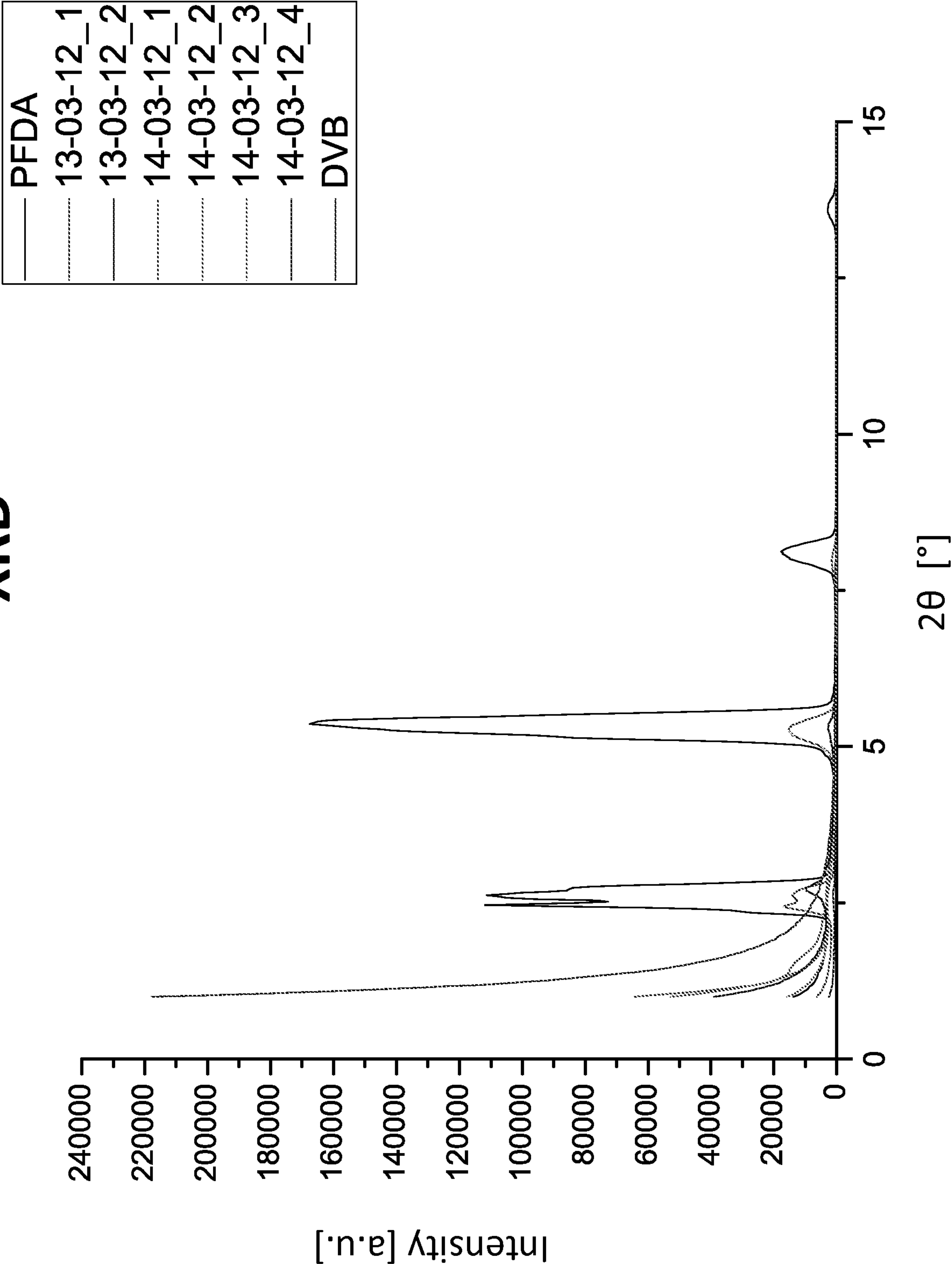


FIG. 15

XRD

Annealing

—	PFDA
---	13-03-12_1_thermal
---	13-03-12_2_thermal
---	14-03-12_1_thermal
---	14-03-1_2_thermal
---	14-03-12_3_thermal
---	14-03-12_4_thermal

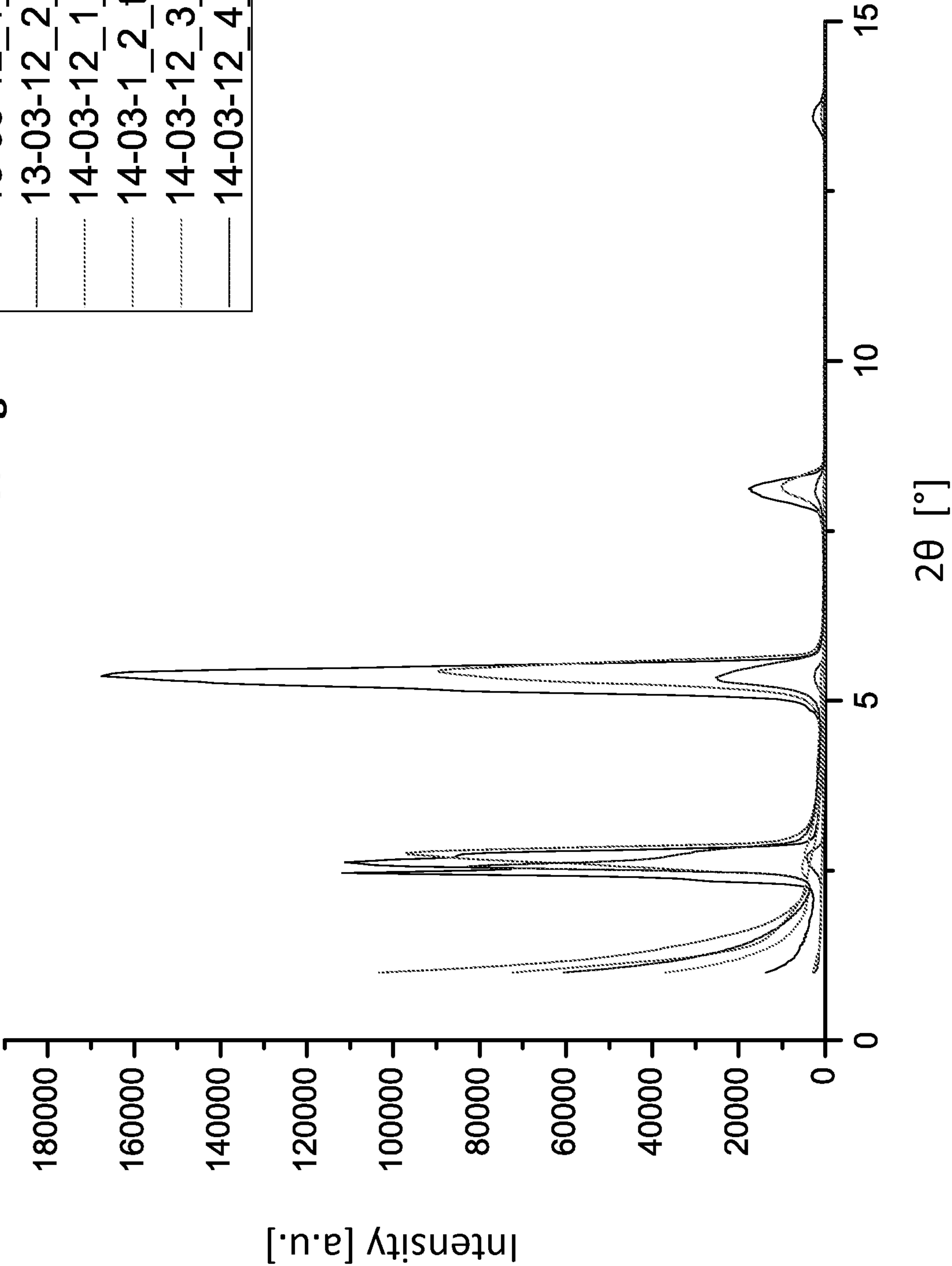


FIG. 16

XRD

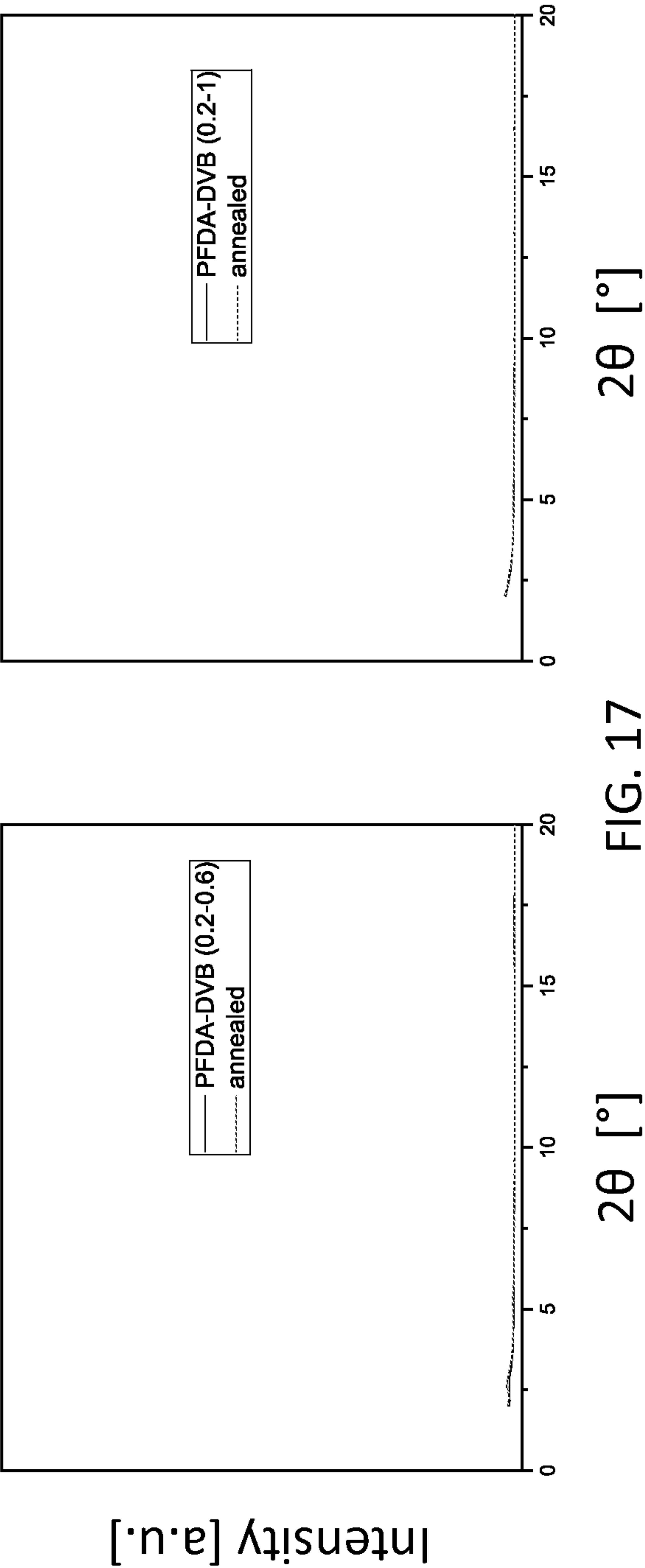
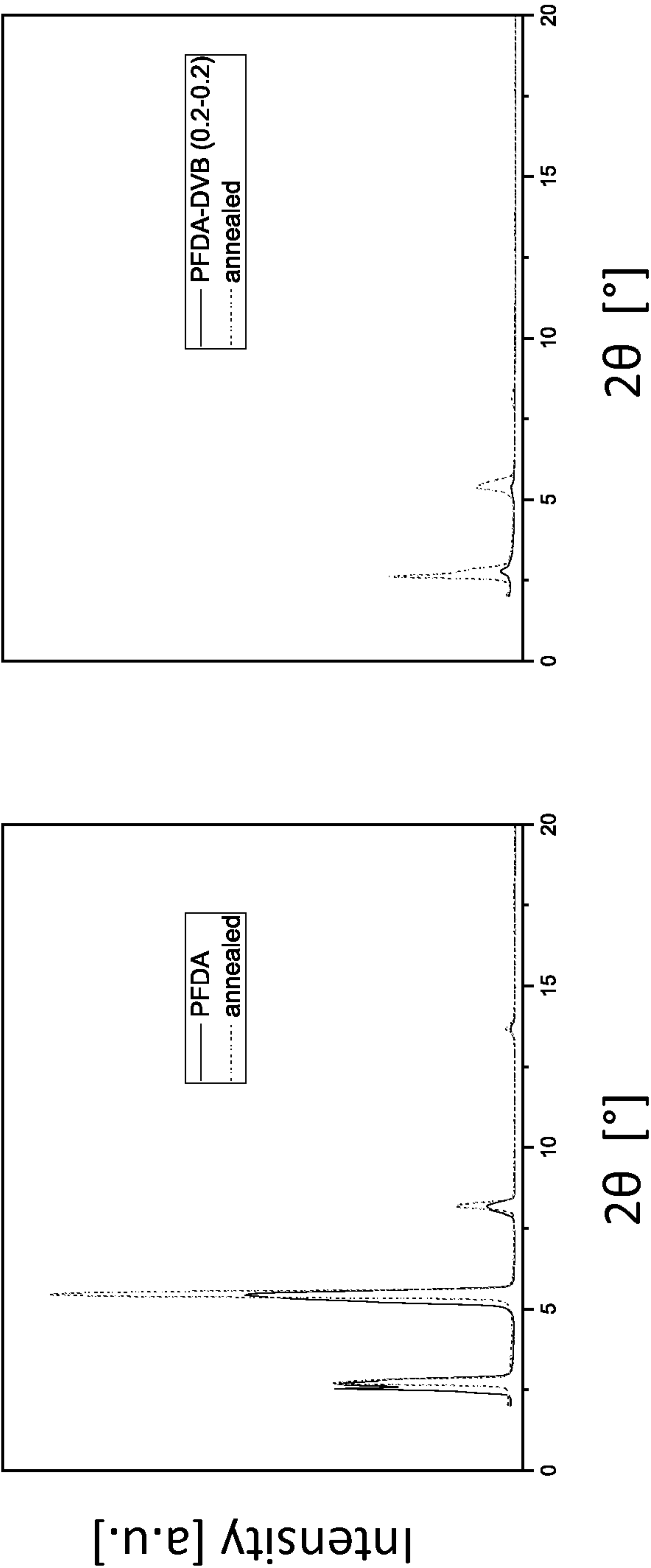


FIG. 17

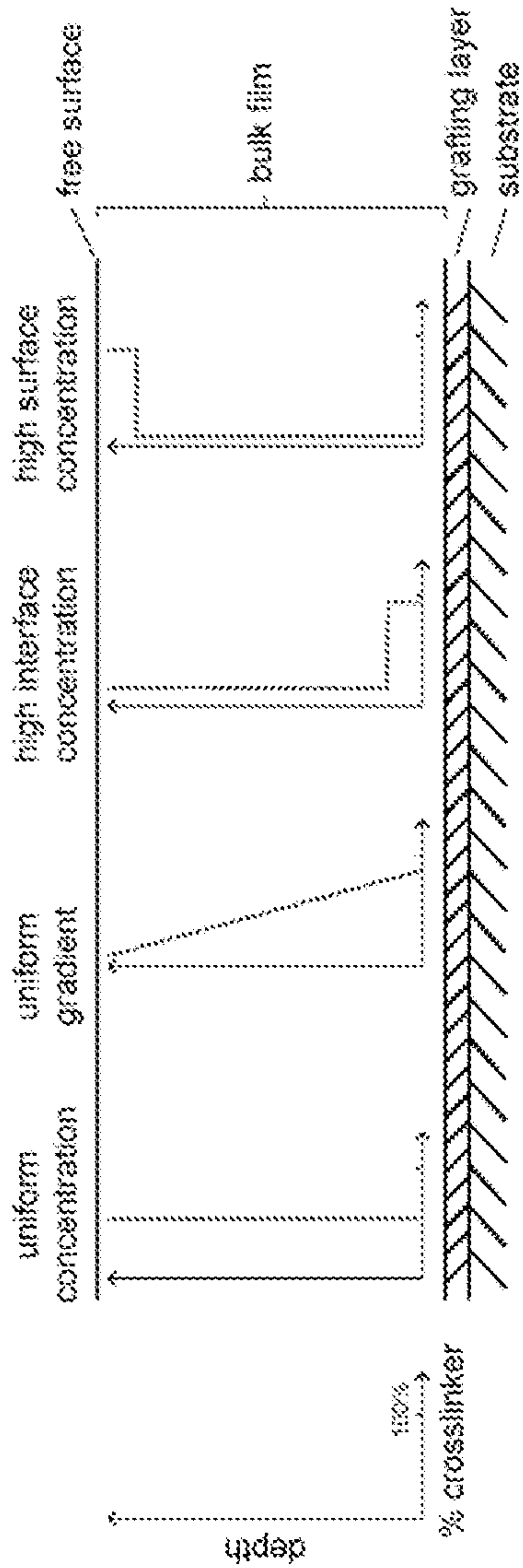


FIG. 18

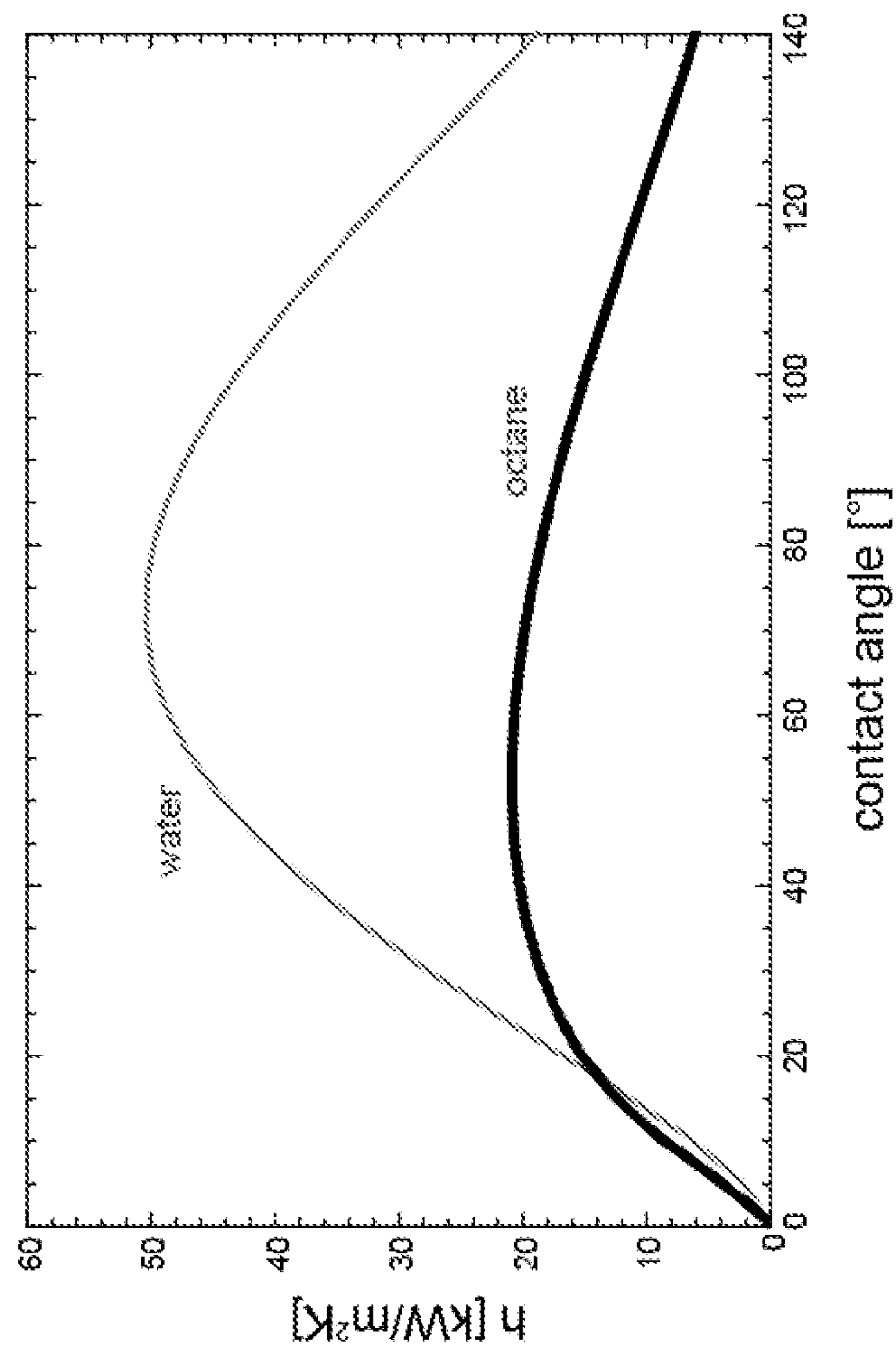
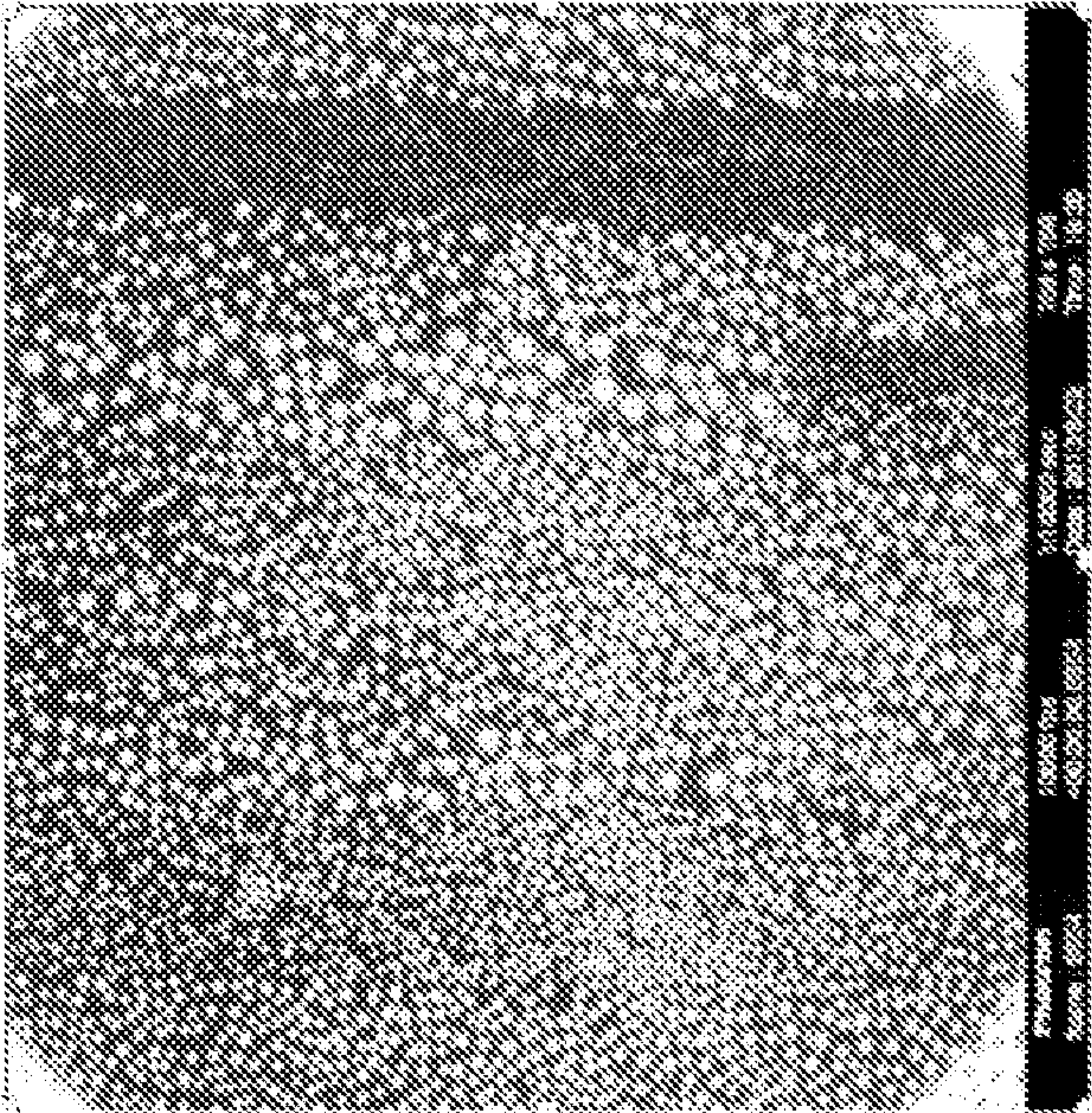


FIG. 19



surface	$\Delta\theta$ [°]	$r_{\max}$ [mm]
fluorosilane	26.7 ± 1.5	2.4 ± 0.1
PFDA-co-DVB	11.0 ± 1.0	1.6 ± 0.6

FIG. 20a

FIG. 20b

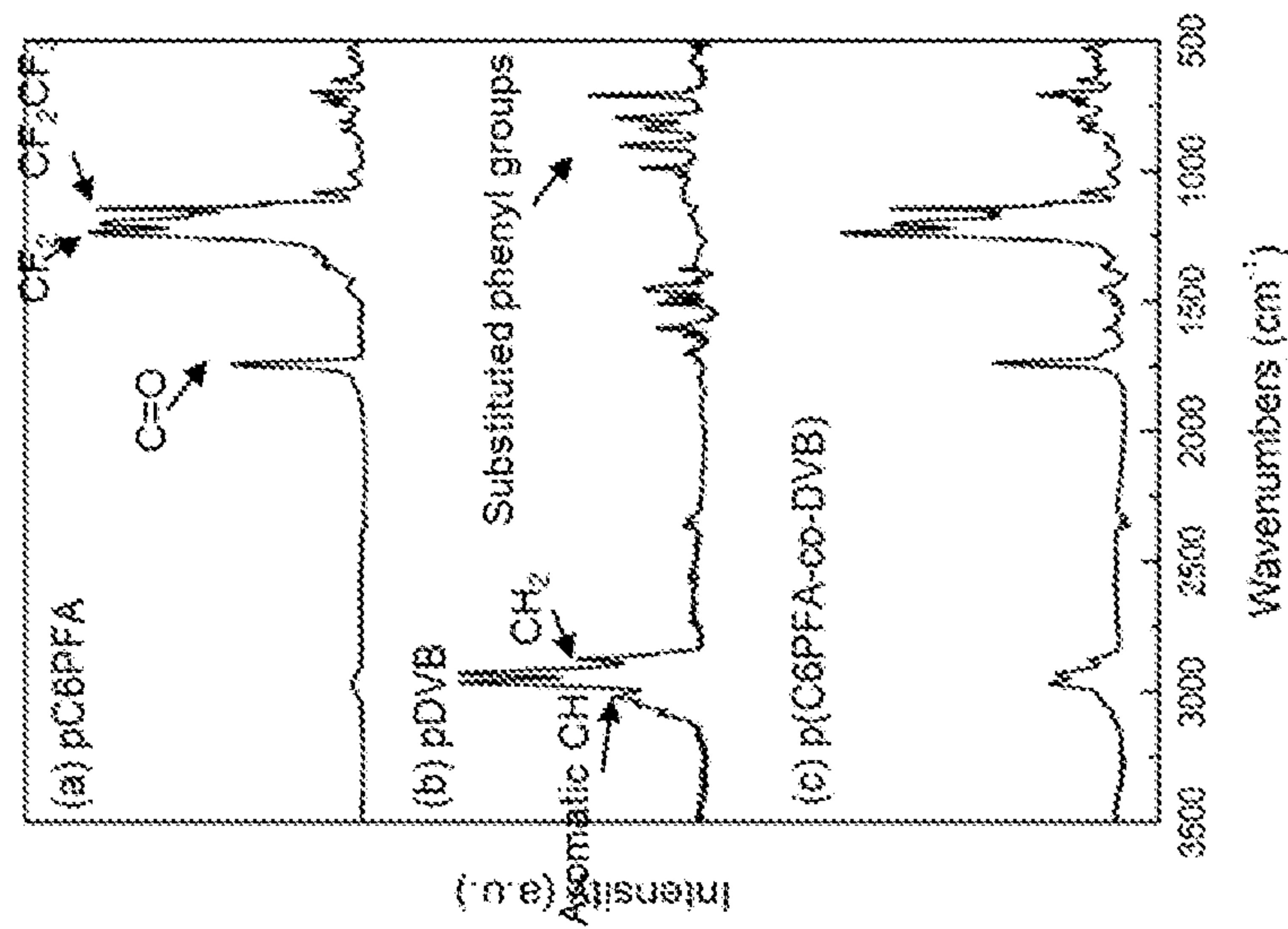


FIG. 21

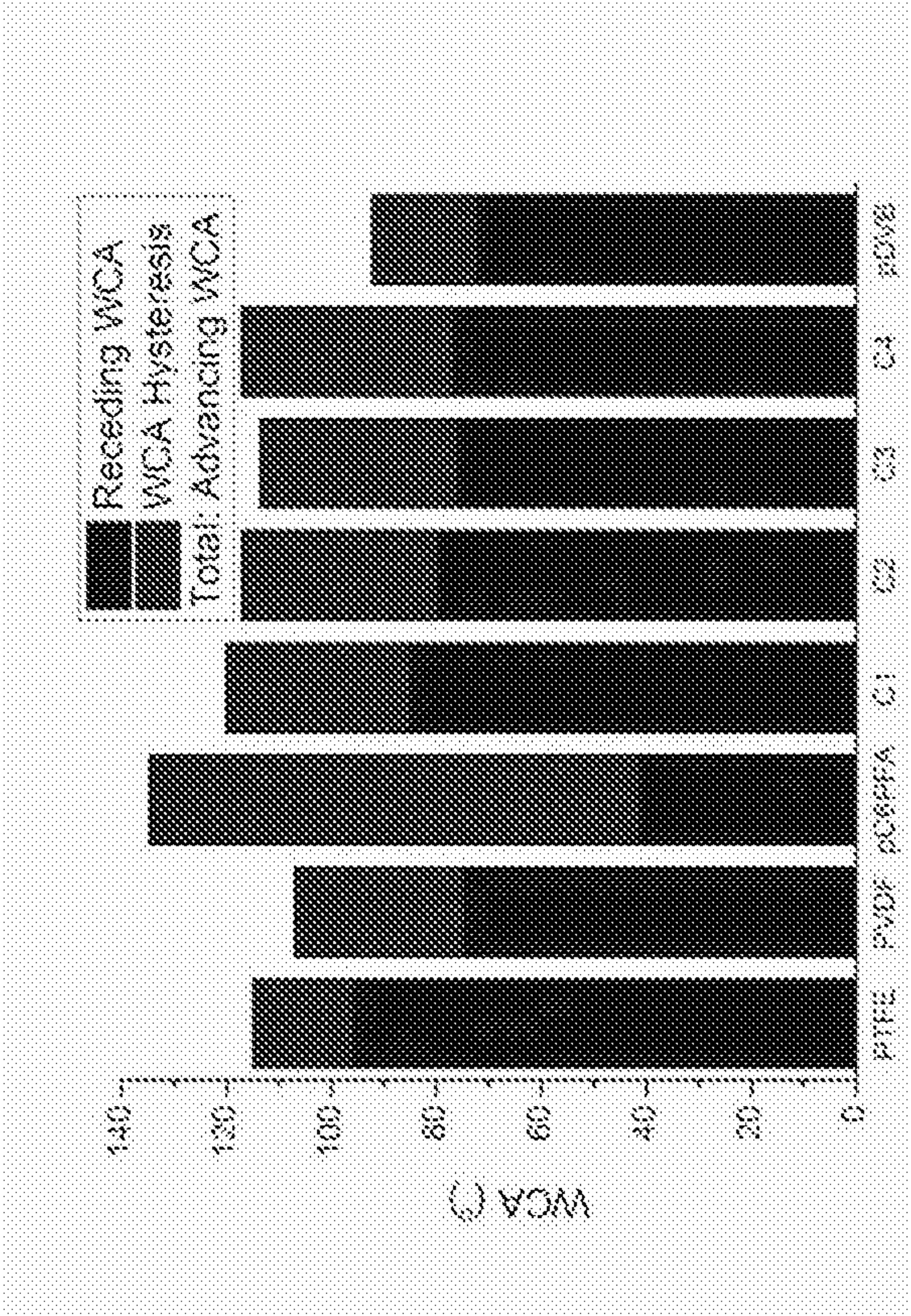


FIG. 22

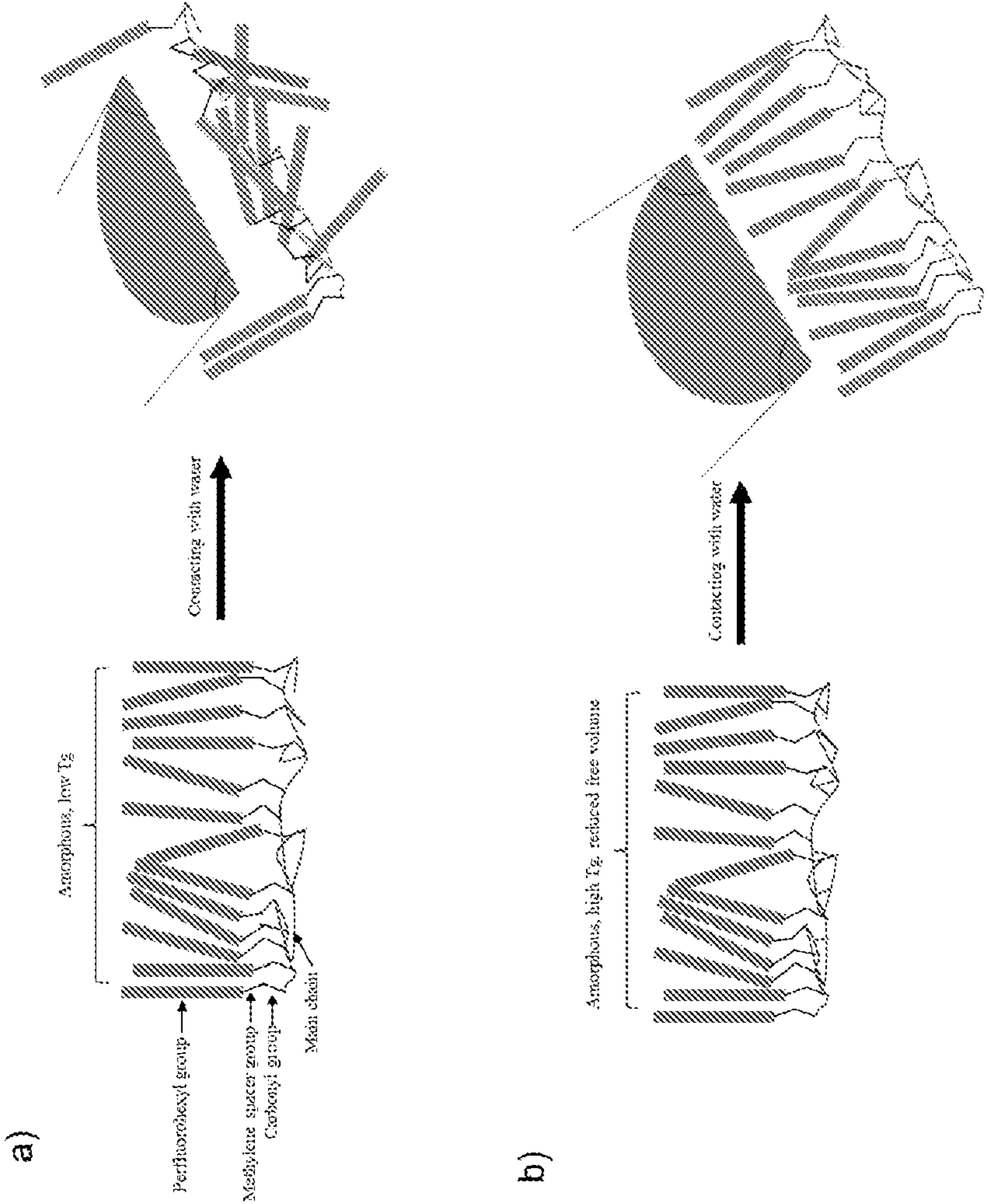


FIG. 23

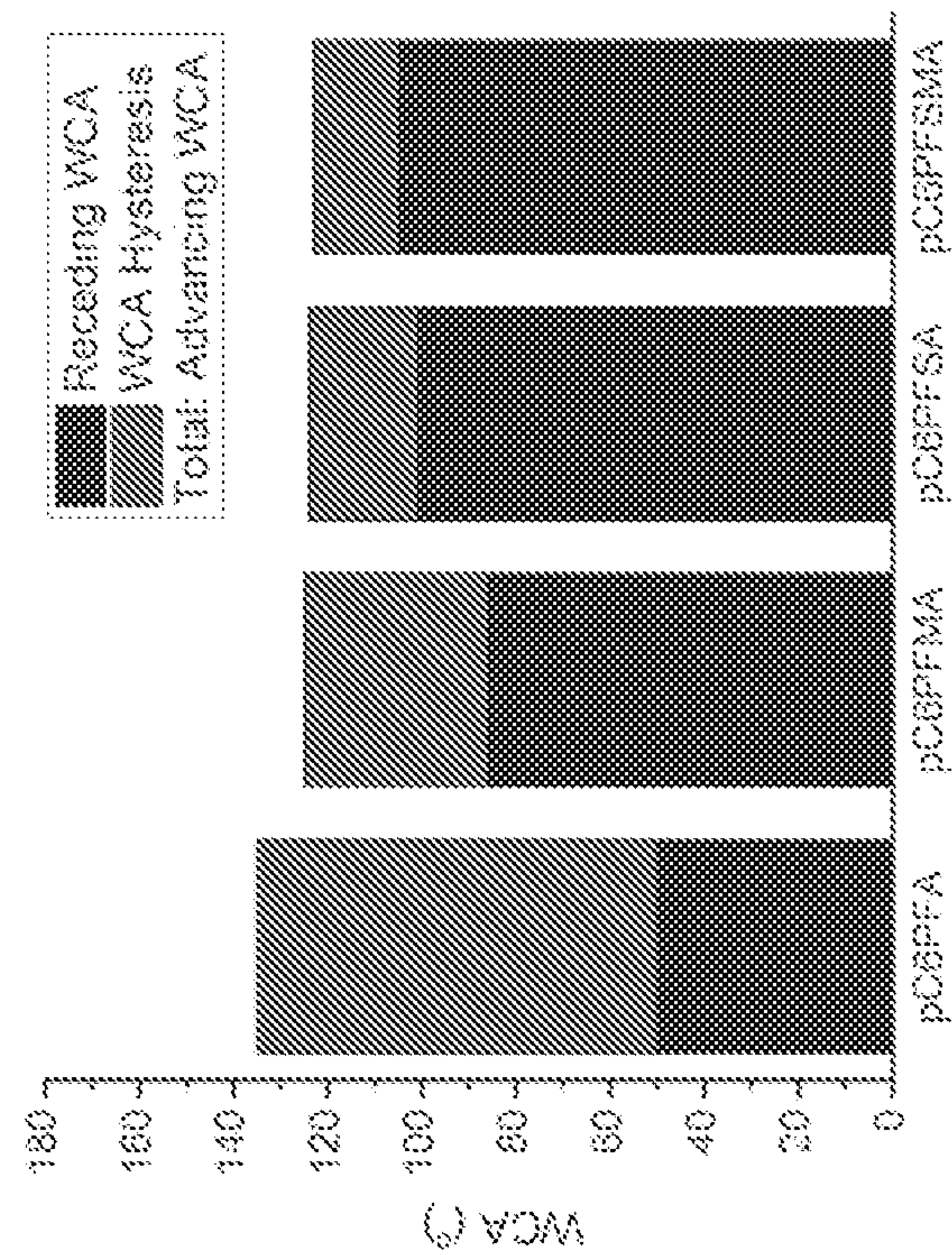


FIG. 24