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- (71) **Applicant: UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC.** [US/US]; 233 Grinter Hall, Gainesville, FL 32611 (US).
- (72) **Inventors: FANG, Yin;** 2841 SW 13th Street, Suite 310, Gainesville, FL 32602 (US). **ASKAR, Khalid;** 1232 SW 14th Ave., Apt. D, Gainesville, FL 32601 (US). **PHIL-LIPS, Blayne, M.;** 2811 SW Archer Road, Apt. B-11, Gainesville, FL 32608 (US). **JIANG, Peng;** 8559 SW 11th Road, Gainesville, FL 32607 (US).
- (74) **Agents: LINDER, Christopher B.** et al.; Thomas / Horstemeyer, LLP, 400 Interstate North Parkway, SE, Suite 1500, Atlanta, GA 30339 (US).
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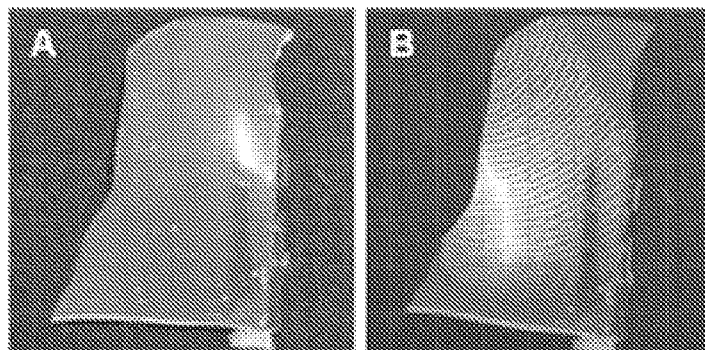


FIG. 1

- (57) **Abstract:** In accordance with the purpose(s) of the present disclosure, as embodied and broadly described herein, embodiments of the present disclosure, in one aspect, relate to porous polymer membranes, structures including porous polymer membranes, devices including porous polymer membranes, methods of using porous polymer membranes, methods of making porous polymer membranes, and the like.

**POROUS POLYMER MEMBRANES, METHODS OF MAKING,
AND METHODS OF USE**

CLAIM OF PRIORITY TO RELATED APPLICATION

5 This application claims priority to co-pending U.S. provisional application entitled
“POROUS POLYMER MEMBRANES, METHODS OF MAKING, AND METHODS OF
USE” having Serial No.: 61/897,848, filed on October 31, 2013, which is entirely incorporated
herein by reference.

BACKGROUND

10 Shape memory polymers are a class of "smart" materials that can memorize and recover
their permanent shapes in response to an external stimulus, such as heat, light, solvent,
electricity, and magnetic fields.¹⁻¹⁵ They have been extensively exploited for a wide spectrum of
technological applications, like smart surgical stents and sutures,¹⁶⁻¹⁷ implants for minimally
15 invasive surgery,¹⁸⁻¹⁹ aerospace morphing structures,²⁰⁻²² sensors and actuators,²³⁻²⁴ and self-
healing materials.²⁵ Compared with their alloy counterparts (e.g., nitinol alloy), SMPs have
gained increased attention due to their dramatically larger strain storage and recovery (up to
800% vs. less than 8%), low cost, light weight, ease of synthesis, and biocompatibility.^{1-2,6-9}
Shape memory (SM) is typically achieved in a three-step process that includes *programming*,
20 *storage*, and *recovery*. Programming involves deforming a sample from its permanent shape to
a temporary shape. This is usually done above the polymer glass transition temperature (T_g) to
take advantage of the compliant nature of SMPs at high temperature. Once the sample has been
deformed, it is cooled below T_g to "freeze" in the temporary shape, which is due to restricted
polymer chain mobility. Recovery occurs when the sample is heated to the vicinity of T_g , which
25 increases chain mobility and allows the polymer to return to its permanent shape via entropy
elasticity.⁶⁻⁹

 The recovery time for thermoresponsive SMPs which are mostly studied and employed
in practical devices is usually long – on the order of minutes.⁷⁻⁹ This greatly impedes many
applications that require fast response speed. Similar slow response is also suffered by other
30 types of SMPs activated through lasers,²⁶ electricity,²⁷ infrared absorption,²⁸ and alternating
magnetic fields.²⁹ Indeed, most of these different SM activation mechanisms are still
thermoresponsive as they depend on the generation of heat to trigger the final shape recovery.
Additionally, "hot" programming (i.e., heating SMP above a transition temperature such as T_g
and then deforming to a temporary configuration) is generally utilized by almost every class of
35 SMPs.¹⁻¹⁵ By contrast, SMPs that can be "cold" programmed (i.e., programming at or below

ambient temperature), which could provide a wide degree of processability to accommodate broader application requirements (e.g., operating at ambient conditions), are rare.³⁰⁻³¹ Moreover, most of current SMP applications focus on leveraging the macroscopic SM effect, where the deformation length -scale is large (on the order of centimeters). Thus, there is a need to overcome these deficiencies.

SUMMARY

In accordance with the purpose(s) of the present disclosure, as embodied and broadly described herein, embodiments of the present disclosure, in one aspect, relate to porous polymer membranes, structures including porous polymer membranes, devices including porous polymer membranes, methods of using porous polymer membranes, methods of making porous polymer membranes, and the like.

An embodiment of the present disclosure provides for a structure, among others, that includes: a porous polymer membrane including an ordered array of voids, wherein the distance between at least two pairs of adjacent voids is substantially the same, wherein a polymer framework separates the voids, wherein when the voids are in a collapsed state the porous polymer membrane is substantially clear, wherein when the voids are in an uncollapsed state the porous polymer membrane has an iridescent color, wherein upon pressure to an area of the collapsed voids, the collapsed voids renew their uncollapsed state, and/or wherein upon exposure to an area of the collapsed void to a solvent, the collapsed voids renew their uncollapsed state.

An embodiment of the present disclosure provides for a method of making a structure, among others, that includes: disposing nanoparticles onto a surface to form an array of nanoparticles; introducing a prepolymer mixture to the array of nanoparticles; polymerizing the prepolymer mixture to form a polymer framework around the array of nanoparticles; and removing the nanoparticles to form an ordered array of voids to form a porous polymer membrane, wherein the distance between at least two pairs of adjacent voids is substantially the same, wherein the polymer framework separates the voids, wherein when the voids are in a collapsed state the porous polymer membrane is substantially clear, wherein when the voids are in an uncollapsed state the porous polymer membrane has an iridescent color.

BRIEF DESCRIPTION OF THE DRAWINGS

Many aspects of the present disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, with emphasis

instead being placed upon clearly illustrating the principles of the disclosure. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

Figure 1 illustrates a photograph of a macroporous ETPTA/PEGDA copolymer membrane (Figure 1A) before fingerprinting and (Figure 1B) after fingerprinting.

Figure 2 illustrates typical SEM images of (Figure 2A) Top-view of a fingerprinted ETPTA/PEGDA copolymer. Figure 2B illustrates cross-section view of a fingerprinted area showing the change of height of a peak-valley transition region. Figure 2C cross-sectional view of a fingerprinted area.

Figure 3 illustrates a photograph of a macroporous ETPTA/PEGDA membrane with printed "light bulb" pattern using a rubber stamp at room temperature.

Figure 4 illustrates a photograph of a macroporous ETPTA/PEGDA membrane with hand-written "FLORIDA" using a traditional pen with ethanol as the ink.

Figure 5 illustrates a specular optical reflection spectra obtained from a plain ETPTA/PEGDA copolymer with collapsed voids, a fingerprinted sample, and an ethanol-treated sample.

Figure 6 illustrates a comparison of two nanoporous ETPTA/PEGDA co-polymer films with (Figure 6A) collapsed nanopores (dried out of water) and (Figure 6B) open nanopores (dried out of ethanol).

Figure 7A illustrates a comparison of specular transmission spectra for a nanoporous ETPTA/PEGDA membrane cyclically dried out of water and ethanol. Figure 7B illustrates a comparison of transmission at 600 nm for the spectra in (Figure 7A).

Figure 8, Scheme 2 is an illustration of the templating procedures for making macroporous polymer membranes by using self-assembled silica colloidal crystals as structural templates.

DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, and as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure,

subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of environmental engineering, biology, chemistry, materials science, mechanical engineering, and the like, which are within the skill of the art.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the probes disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.), but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by volume, temperature is in °C, and pressure is at or near atmospheric. Standard temperature and pressure are defined as 20 °C and 1 atmosphere.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequences where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a compound” includes a plurality of compounds. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

Discussion

In accordance with the purpose(s) of the present disclosure, as embodied and broadly described herein, embodiments of the present disclosure, in one aspect, relate to porous polymer membranes, structures including porous polymer membranes, devices including porous polymer membranes, methods of using porous polymer membranes, methods of making porous polymer membranes, and the like.

In an embodiment, the porous polymer membrane can be used as a pressure-responsive shape memory polymer, where the mechanical properties of the porous polymer membrane can be tuned by controlling the ratio of the co-polymers used to form the porous polymer membrane. In particular, the porous polymer membrane includes an array of voids that are in a collapsed state (*e.g.*, the volume of the void is reduced close to 0) or a disordered state (*e.g.*, the voids are not highly ordered in three-dimension), and when a pressure or solvent is applied to an area of the porous polymer membrane, the collapsed or disordered voids recover in that area return to their uncollapsed or highly ordered state or fully formed state (*e.g.*, having maximum void volume). In this way, the porous polymer membrane can take on the shape of what caused the pressure (*e.g.*, a finger print touch) or where the solvent was controllably disposed on the porous polymer membrane. In addition, when the voids are in a collapsed state, the porous polymer membrane is substantially transparent (*e.g.*, a pale white color) or transparent, while when the voids have recovered from the collapsed state, the porous polymer membrane has an iridescent color that can be tuned by altering the volume of the voids. In an embodiment, the porous polymer membrane has shape memory characteristics and tunable diffraction properties. An embodiment of the present disclosure provides for a SMP that enables unusual "cold" programming and instantaneous shape recovery triggered by applying an external pressure or exposing to an organic solvent (*e.g.*, ethanol) at ambient conditions.

An advantage of an embodiment of the present disclosure is that the process for making the porous polymer membranes is simple, scalable, and inexpensive. In addition, embodiments of the present disclosure can be used in applications such as tunable diffractive optical devices, finger printing for biometric recognition (*e.g.*, with both shape recognition and color change), tunable anti-glare coatings, biomedical devices (*e.g.*, tunable polymer stents), pressure/vapor sensors, aerospace morphing structures, and the like.

In an embodiment, the porous polymer membrane can include an ordered three dimensional array of voids, where a polymer framework separates the voids. As mentioned above, the porous polymer membrane is substantially transparent or semi-transparent when the voids are in a collapsed or a disordered state. And the porous polymer membrane has an

iridescent color that can be changed by altering the volume of the voids when the voids have recovered from the collapsed state. In an embodiment, the void can be collapsed by drying the voids after formation or exposing the voids to water and then evaporating the water from the porous polymer membrane. The voids collapse due to capillary forces when the water
5 evaporates.

In an embodiment, the collapsed voids can be renewed by applying pressure to an area of the porous polymer membrane. In an embodiment, one area of the porous polymer membrane has pressure applied to it, while another area does not have pressure applied to it. The voids are renewed in the area having the applied pressure, while the voids are not renewed in areas where
10 no pressure was applied. In addition, the areas that had pressure applied to it have an iridescent color, while the other areas do not.

In an embodiment, the collapsed voids can be renewed by exposing an area of the porous polymer membrane to a solvent such as methanol, ethanol, isopropanol, acetone, butanol, and a combination thereof. In an embodiment, one area of the porous polymer membrane is exposed to
15 a solvent, while another area is not exposed to a solvent. The voids are renewed in the area exposed to the solvent, while the voids are not renewed in areas not exposed to the solvent. In addition, the areas exposed to the solvent have an iridescent color, while the other areas do not.

The thickness of the porous polymer membrane varies depending on the state of the voids and the number of voids along a plane perpendicular to the length of the porous polymer membrane. In an embodiment the porous polymer membrane can have a thickness of about 1
20 micrometer to 300 micrometers.

In an embodiment, the polymer framework can include a co-polymer of a pair of acrylate monomers that have low glass transition temperatures ($T_g < \text{room temperature}$). In an embodiment, the polymer framework is a co-polymer of ethoxylated trimethylolpropane triacrylate (ETPTA) and polyethylene glycol diacrylate (PEGDA), the structures of which are
25 shown in Example 1. Both ETPTA and PEGDA are flexible at room temperature. The mechanical properties (*e.g.*, rigidity and strength) of the resulting co-polymers can be tuned by controlling the ratio of these two monomers. A higher ratio of PEGDA leads to a softer polymer. In an embodiment, the ratio of ETPTA and PEGDA can be about 1:2 to 1:6.

In an embodiment, the porous polymer membrane can include an ordered array of voids. In an embodiment, the voids can be stacked directly on top of one another or the stacking can be offset. In an embodiment, the thickness of the porous polymer membrane can include about 1 to
30 100 monolayers of voids.

In an embodiment, the distance between at least two pairs of adjacent voids is
35 substantially the same (*e.g.*, about 100 nm to 1000 nm). In an embodiment, the number of

unique pairs can be about 10, 100, 1000, 10,000, 100,000, 1,000,000, 100,000,000, 100,000,000, to about 10, 100, 1000, 10,000, 100,000, 1,000,000, 100,000,000, 100,000,000, 1×10^{10} , 1×10^{12} , 1×10^{15} , 1×10^{17} , or 1×10^{20} and any set of ranges (*e.g.*, about 10,000 to 100,000, about 100 to 1×10^{10} , etc.) within these numbers or subranges (*e.g.*, about 15 to 200,000, 2,500,000 to 3×10^{12} , etc.) within these numbers.

In an embodiment, the distance between each pair of adjacent voids is substantially the same. In an embodiment, the distance between a portion of the pairs of adjacent voids is substantially the same. In an embodiment, the “portion” can be about 50% or more, about 60% or more, about 70% or more, about 80% or more, about 90% or more, about 99% or more, or about 100%, over a defined area of the porous polymer layer. In an embodiment, the defined area can include about 50% or more, about 60% or more, about 70% or more, about 80% or more, about 90% or more, about 95% or more, about 99% or more, or about 100%, of the area of the porous polymer layer. The term “substantially” in these contexts can mean about 50% or more, about 60% or more, about 70% or more, about 80% or more, about 90% or more, about 99% or more, or about 100%. The term “adjacent” refers to two voids next to one another without a void separating them in the same porous polymer membrane.

In an embodiment, a polymer framework separates the voids. In an embodiment, the diameter of substantially all of the voids can be substantially equivalent. In an embodiment, the diameter is about 0.03 micrometers to 10 micrometers. The term “substantially” in this context can mean about 50% or more, about 60% or more, about 70% or more, about 80% or more, about 90% or more, about 99% or more, or about 100%.

In an embodiment, two sets of voids of different diameters can be present that form an ordered array of voids. In an embodiment, a first set of a pair of voids has a first diameter and a second set of a pair of voids has a second diameter, where the first diameter and the second diameter are not the same. The ordered array of voids can have a plurality of first sets and second sets. In another embodiment, the porous polymer membrane can include three or more sets of such voids each having different diameters.

In an embodiment, the porous polymer membrane is formed by disposing nanoparticles onto a surface to form an array of nanoparticles. In an embodiment, a monomer mixture can be disposed on a surface using capillary forces (See Example) or using a process such as a doctor blade coating process, tape casting, or applying a simple shear force by two plates with a controlled gap in between. The nanoparticles can be aligned in a three dimensional ordered colloidal crystal array, *e.g.*, the particles can be located in crystalline lattices of, for example, a face-centered cubic (f.c.c.), hexagonal-centered cubic (h.c.p.) crystals, or the like. After the monomer mixture is disposed on the nanoparticle array, the monomer mixture can be

polymerized to form a co-polymer membrane having nanoparticles disposed in the polymer membrane. In an embodiment, the polymerization can be photopolymerization, thermopolymerization, or a combination thereof.

Subsequently, a portion (*e.g.*, about 50%, 60%, 60%, 80%, 90%, 95%, 99% or more, or about 100%) or all of the nanoparticles can be removed to form the porous polymer membrane. In an embodiment, the nanoparticles can be removed by a process that does not alter the polymer. The type of process used to remove the nanoparticles depends, at least in part, upon the type of nanoparticle and the polymer. In an embodiment, the porous polymer membrane is formed by dissolving the nanoparticles using an acid solution such as, but not limited to, hydrofluoric acid (*e.g.*, for silica nanoparticles). The porous polymer membrane including an array of voids is formed once the nanoparticles are removed.

As mentioned above, the voids are made from the removal of one or more nanoparticles. In an embodiment, the nanoparticles are disposed on top of one another in the polymer membrane, and when the nanoparticles are removed, a void is formed in the place of each nanoparticle. In an embodiment, the voids are distinct from one another and in another embodiment the voids are interconnected to form interconnected volumes that can form channels within and/or through the porous polymer membrane.

In an embodiment the monomer mixture can include two or more acrylate monomers such as those described herein, wherein each monomer can be about 5 to 95 weight percent of the monomer mixture. In an embodiment the prepolymer mixture can include an ethoxylated trimethylolpropane triacrylate (ETPTA) and a polyethylene glycol diacrylate (PEGDA). In an embodiment, the volumetric ratio of ETPTA to PEGDA can be about 1:1 to 1:10 or about 1:2 to 1:6. In addition, the monomer mixture can include a polymer initiating agent such as a photoinitiator (*e.g.*, 2-hydroxy-2-methyl-1-phenyl-1-propanone, azobisisobutyronitrile, or and 2,2-dimethoxy-2-phenylacetophenone). The amount of initiator used depends upon the polymerization process, the monomers, and the like.

Once the monomer is polymerized, a polymer framework is formed around the nanoparticles. After the nanoparticles are removed, the polymer framework supports the porous polymer membrane. The mechanical characteristics of the polymer framework can be controlled by selection of the monomers, the ratio of the monomer, and the like. The dimensions of the polymer framework can be controlled by the process of disposing the monomer/nanoparticle mixture on the substrate. In an embodiment, the thickness of the polymer framework between adjacent nanoparticles can be about 100 nm to 1000 nm.

In an embodiment, the nanoparticles can be of the same or different type and/or same or different size, depending on the use or purpose of the porous polymer membrane. The selection

of the type nanoparticle can depend upon the process for removing the nanoparticle, the type of polymer, and/or polymer framework. The selection of the size can depend upon the process for removing the nanoparticles, the type of polymer, the polymer framework, the diameter of the desired voids and channel, and the like. In an embodiment, two or more different types and/or sizes of nanoparticles can be selected. In an embodiment, two or more processes can be used to remove nanoparticles (*e.g.*, when two or more types of nanoparticles are used in the monomer/nanoparticle mixture). The type of nanoparticle can include silica nanoparticles, polymer latex nanoparticles, titania nanoparticles, CdSe nanoparticles, and other nanoparticles where the type selected has a uniform diameter. In an embodiment, the nanoparticles can have a diameter of about 100 to 1000 nm or about 200 to 500 nm.

Once the nanoparticles have been removed, the voids can be collapsed by exposing the porous polymer membrane to water and then evaporating the water. Capillary forces will cause the voids to collapse. It should also be noted that once the voids are renewed so that they are not collapsed, exposing the voids to water and then evaporating the water will cause the voids to collapse again. Thus, the porous polymer membrane can be renewed.

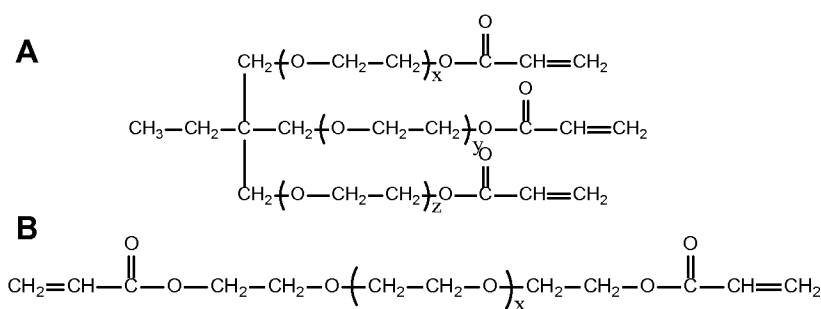
Examples

Now having described the embodiments of the present disclosure, in general, example 1 describes some additional embodiments of the present disclosure. While embodiments of the present disclosure are described in connection with example 1 and the corresponding text and figures, there is no intent to limit embodiments of the present disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

Example 1

Shape memory polymers (SMPs) are a class of "smart" materials that offer mechanical actions triggered by an external stimulus, such as heat, light (*e.g.*, ultraviolet light), solvent, and electromagnetic fields. These materials have the ability to "memorize" a macroscopic permanent shape, be manipulated and fixed to a temporary shape under specific conditions (*e.g.*, at a specific temperature), and then later relax to the original, stress-free conditions under various external commends. They have found important technological applications in a spectrum of fields ranging from smart biomedical devices to self-healing materials. Although pressure is an important parameter in many industrial processes, pressure-responsive SMPs are rare. In this Example a new type of SMP that can be triggered by a small pressure change and/or a solvent is described.

The chemical compositions of pressure-sensitive SMPs can vary depending on the desired characteristics of the SMP. In an embodiment, the composition can include various volumetric ratios of two monomers - ethoxylated trimethylolpropane triacrylate (ETPTA) and polyethylene glycol (600) diacrylate (PEGDA). These two chemicals are both from Sartomer and their product numbers are SR 415 and SR 610. Their molecular structures are shown in Scheme 1. The glass transition temperature of the corresponding polymers is -40°C for ETPTA and -42°C for PEGDA. The volumetric ratio of ETPTA to PEGDA can be varied from 1:2 to 1:6. 0.5% (weight) Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone) is added to the monomer mixture as the photoinitiator. The monomers can be easily photopolymerized by exposed to ultraviolet radiation by using a pulsed UV curing system (RC 742, Xenon). The mechanical properties (*e.g.*, rigidity) of the resulting co-polymers can be tuned by controlling the ratio of these two monomers. A higher ratio of PEGDA leads to a softer polymer.



Scheme 1. Chemical structures of ETPTA (A) and PEGDA (B).

The discovery of the pressure-responsive shape memory properties of the ETPTA/PEGDA co-polymers is based on macroporous co-polymer membranes prepared by a colloidal crystal templating technology. Scheme 2 (Figure 8) shows the illustration of the templating procedures for making macroporous ETPTA/PEGDA films. A silica colloidal crystal having monodispersed 300 nm silica particles is first assembled by a convective self-assembly technology on the surface of a glass microslide. A sandwich cell is then assembled by covering the silica colloidal crystal-coated glass substrate with another glass microslide. The ETPTA/PEGDA monomer mixture is then introduced into the sandwich cell by capillary force. The monomers are then photopolymerized by UV radiation for 4 seconds. The two glass microslides and the silica particles can then be removed by dipping the sandwich cell in a 0.5 vol.% hydrofluoric acid aqueous solution for more than 4 hours. This results in the formation of self-standing macroporous co-polymer membranes after blow-drying the films.

The templated macroporous ETPTA/PEGDA membranes contain three-dimensionally ordered voids originated from the templating silica particles when the membranes are immersed

in water. This is confirmed by the iridescent colors of the wet membranes caused by the Bragg diffraction of visible light from the 3-D ordered crystalline structure. However, the dried copolymer membranes do not show iridescent colors (Figure 1A). This is caused by the collapsing of the nanopores during the evaporation of water trapped into the voids. The strong capillary force induced by the large surface tension of water collapses the voids, making the final membranes nearly transparent. When the copolymer membrane is touched by a finger (a very small pressure is applied like in the typical finger printing process), a clear colorful fingerprint is left on the surface of the macroporous membrane (Figure 1B). The color of the fingerprinted area is controlled by the void size of the templating silica particles. For instance, the sample in Figure 1B templated from 300 nm silica spheres shows iridescent green color in the fingerprinted areas; while a sample consisting of 400 nm voids will show a red color.

The iridescent color of the fingerprinted areas is caused by the Bragg diffraction of visible light from the 3-D ordered voids in the templated macroporous membrane. This is confirmed by the scanning electron microscope images of the sample shown in Figure 2. Figure 2A shows the top-view SEM image of the surface of a fingerprinted sample. The fingerprints are easily perceived from the image (similar to the optical microscope image shown in Figure 1B). The contrast in SEM is coming from the height difference of the peaks and valleys of the fingerprinted areas. The cross-sectional SEM image in Figure 2B is focused on a fingerprinted area. The gradual height change of the fingerprint is clearly evident in the image. The 3-D crystalline order of the 300 nm voids is shown by the cross-sectional SEM image in Figure 2C. The SEM images in Figure 2 explain the appearance of the iridescent colors produced by the fingerprinting process. As the ETPTA/PEGDA copolymers are pressure-responsive SMPs, the permanent shape of the original polymer during photopolymerization (i.e., spherical voids) is memorized during the void collapse caused by water evaporation. When a small pressure is applied, the pressure is sufficient to trigger the recovery of the temporary shape (collapsed voids) into the original one (spherical voids). However, the unpressed regions remain the temporary state, showing no iridescent color.

To further confirm the recovery of the spherical voids is caused by pressure instead of the body temperature of the finger, we used a rubber stamp with adjustable patterns to print the patterns onto the macroporous ETPTA/PEGDA membranes at room temperature. Figure 3 shows the printed patterns using a small pressure (similar to the typical pressure used in common fingerprinting). The colorful "light bulb" pattern on the rubber stamp is clearly shown on the polymer surface.

Instead of pressure, we found that various solvents including methanol, ethanol, isopropanol, and acetone can also trigger the recovery of the collapsed voids into their original

spherical shape. Figure 4 shows a photograph of a macroporous ETPTA/PEGDA membrane with a handwritten "FLORIDA" using a traditional pen with pure ethanol as the ink. Further SEM examination (not shown here) demonstrates the 3-D ordering of spherical voids as the fingerprinted one shown in Figure 2C.

5 The optical properties of the fingerprinted and ethanol-treated macroporous ETPTA/PEGDA membranes are evaluated using a ultraviolet/visible spectrometer. Figure 5 compares the specular optical reflection spectra obtained from a plain co-polymer membrane with collapsed voids after drying out of water (see Figure 1A), the fingerprinted region in Figure 1B, and the ethanol-written region in Figure 4. The collapsed sample does not show apparent
10 diffraction peaks as the voids are collapsed. By contrast, the fingerprinted and the ethanol-treatment samples both show clear Bragg diffraction peaks around 510 nm. This corresponds well to the shining greenish color shown by both samples.

Besides the tunable diffraction properties shown by the pressure- and solvent-sensitive SMPs, which is highly useful for many tunable optical devices such as optical filters and tunable
15 lasers, we further demonstrated another useful application of the novel SMPs in tuning optical reflection (for anti-reflection applications) by controlling the collapsing/opening of the templated voids. In this approach, monolayer colloidal silica nanoparticles with ~100 nm diameter are first self-assembled at an air/water interface and then the colloidal monolayers are transferred onto a glass surface. The same templating procedures as shown in Scheme 2 (Figure
20 8) are then applied to make nanoporous ETPTA/PEGDA membranes. When the co-polymer films are dried out of water, the nanopores are collapsed due to large capillary forces, resulting in high optical reflection at the polymer/air interface. By contrast, by immersing the same film in ethanol and then dried in air, the voids retain the permanent spherical shape, leading to reduced optical reflection (and high optical transmission through the membrane). Figure 6
25 compares the reflection from a SMP membrane with collapsed (dried out of water) and open (dried out of ethanol) nanopores. The good anti-glare performance of the film with open nanopores is evident. The membranes can be consecutively dried out of water and ethanol, resulting in cycling low and high optical transmission as shown in Figure 7.

In summary, we have discovered a new type of shape memory polymer that is a co-
30 polymer of two acrylates. By controlling the ratio of these acrylates, the mechanical properties of the resulting co-polymers can be tuned. The recovery of the permanent shape of these novel SMPs can be easily triggered by applying a small pressure or using some specific solvents. The potential applications of this novel type SMP in tunable diffractive optical devices, color fingerprinting, and tunable anti-glare coatings have been demonstrated.

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It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (*e.g.*, 1%, 2%, 3%, and 4%) and the sub-ranges (*e.g.*, 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term “about” can include traditional rounding according to significant figures of the numerical value. In addition, the phrase “about ‘x’ to ‘y’” includes “about ‘x’ to about ‘y’”.

It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are set forth only for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiments of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure.

25

CLAIMS

We claim:

1. A structure comprising:

5 a porous polymer membrane including an ordered array of voids, wherein the distance between at least two pairs of adjacent voids is substantially the same, wherein a polymer framework separates the voids, wherein when the voids are in a collapsed state the porous polymer membrane is substantially clear, wherein when the voids are in a uncollapsed state the porous polymer membrane has an iridescent color, wherein upon pressure to an area of the collapsed voids, the collapsed voids renew their uncollapsed state, and wherein upon exposure to an area of the collapsed void to a solvent, the collapsed voids renew their uncollapsed state.

2. The structure of claim 1, wherein the distance between each pair of adjacent voids is substantially the same.

3. The structure of claim 1, wherein the distance between 50% of the pairs of adjacent voids is substantially the same.

4. The structure of claim 1, wherein the distance between 75% of the pairs of adjacent voids is substantially the same.

5. The structure of claim 1, wherein the distance between 90% of the pairs of adjacent voids is substantially the same.

6. The structure of claim 1, wherein the number of unique pairs is about 10 to 1×10^{20} .

7. The structure of claim 1, wherein each void has a diameter that is about the same.

8. The structure of claim 1, wherein the diameter of the void is about 100 nm to 1000 nm.

9. The structure of claim 1, wherein the diameter of the voids are substantially the same.

10. The structure of claim 1, wherein the polymer framework is a co-polymer of ethoxylated trimethylolpropane triacrylate (ETPTA) and polyethylene glycol diacrylate (PEGDA).

11. The structure of claim 1, wherein the porous polymer membrane has a thickness of about 1 micrometer to 300 micrometers.

12. A method of making a structure, comprising:

5 disposing nanoparticles onto a surface to form an array of nanoparticles;
introducing a prepolymer mixture to the array of nanoparticles;
polymerizing the prepolymer mixture to form a polymer framework around the
array of nanoparticles; and

10 removing the nanoparticles to form an ordered array of voids to form a porous
polymer membrane, wherein the distance between at least two pairs of adjacent voids is
substantially the same, wherein the polymer framework separates the voids, wherein
when the voids are in a collapsed state the porous polymer membrane is substantially
clear, wherein when the voids are in an uncollapsed state the porous polymer membrane
has an iridescent color.

13. The method of claim 12, wherein the nanoparticles are silica nanoparticles.

14. The method of claim 12, wherein the polymer framework is a co-polymer of ethoxylated
trimethylolpropane triacrylate (ETPTA) and polyethylene glycol diacrylate (PEGDA).

15. The method of claim 12, wherein the prepolymer mixture includes an ethoxylated
trimethylolpropane triacrylate (ETPTA) and a polyethylene glycol diacrylate (PEGDA).

16. The method of claim 12, wherein removing includes dissolving the nanoparticles.

17. The method of claim 12, further comprising: drying the porous polymer membrane,
wherein the void collapse so that the porous polymer membrane is substantially clear.

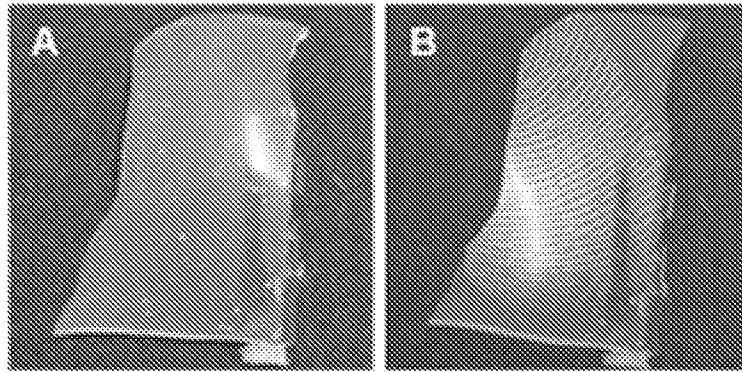


FIG. 1

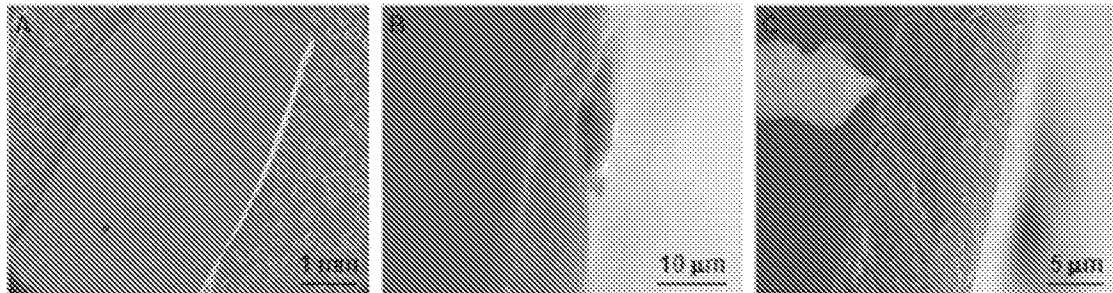


FIG. 2

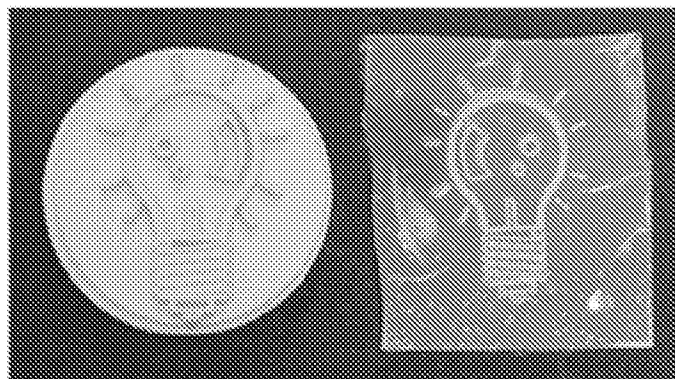


FIG. 3

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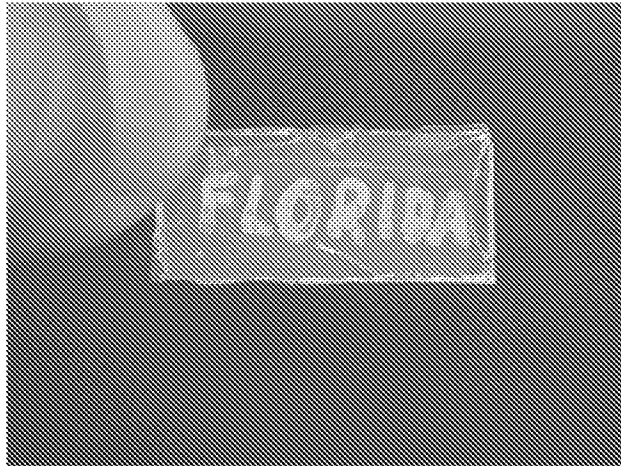


FIG. 4

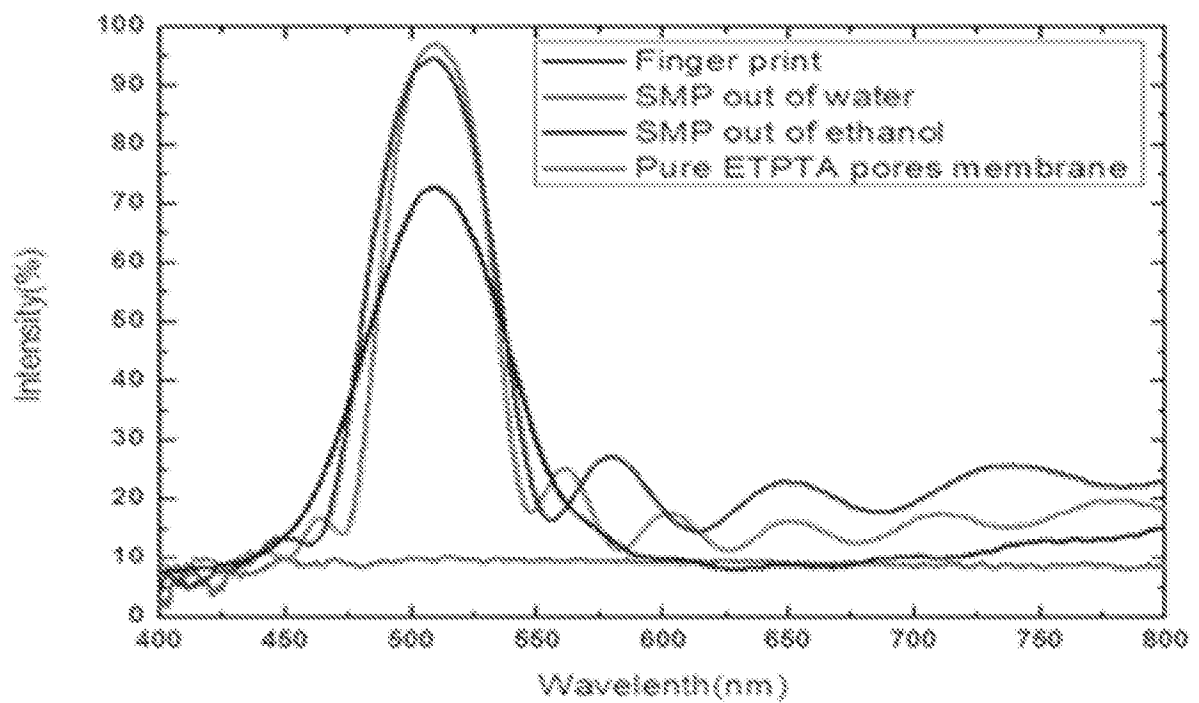


FIG. 5

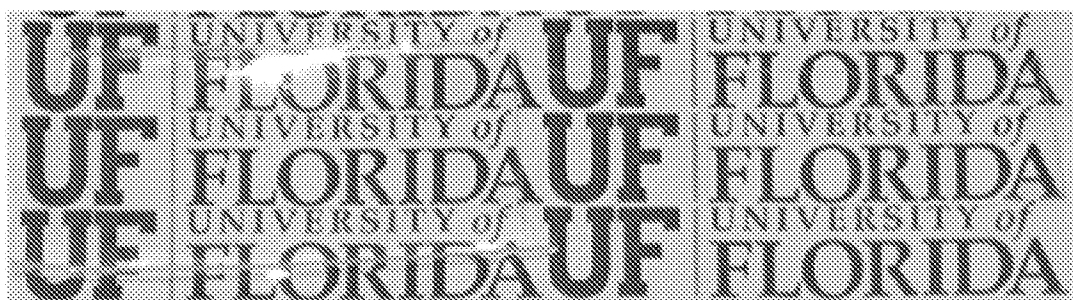


FIG. 6

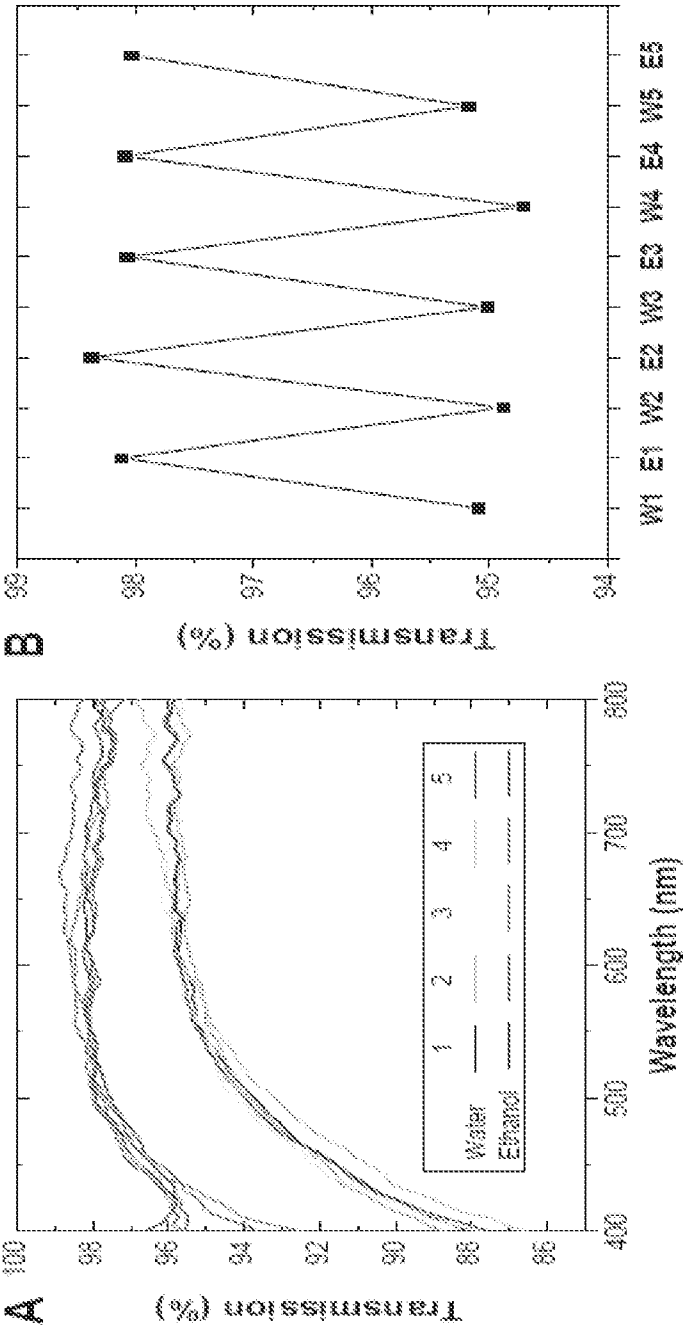


FIG. 7

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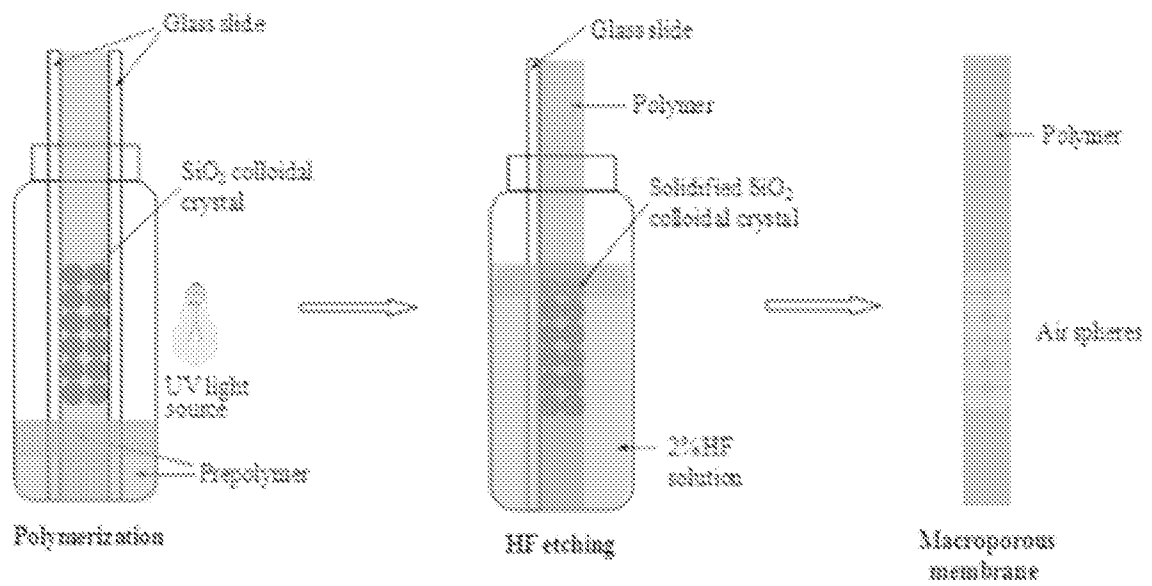


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2014/063172

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - C08J 9/26 (2014.01) CPC - C08J 9/26 (2014.11) According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC(8) - C08J 9/26 (2014.01) CPC - C08J 9/26 (2014.11) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched USPC - 427/243 (keyword delimited) Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Orbit, Google Patents, Google Scholar, Google. Search terms used: ETPTA PEGDA PEGA silica nanoparticles porous polymer membrane voids transparent iridescent		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/0199995 A1 (JIANG et al) 08 August 2013 (08.08.2013) entire document	1-9, 11-13, 16-17
Y		10, 14-15
Y	VELAVAN. Langmuir-Blodgett assembly of yeast cells and colloidal particles. Thesis, May 2013. [retrieved on 22.12.2014]. Retrieved from the Internet. <URL:http://ufdcimages.uflib.ufl.edu/UF/E0/04/55/73/00001/VELAVAN_H.pdf>. entire document	10, 14-15
☐ Further documents are listed in the continuation of Box C. ☐		
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Date of the actual completion of the international search 22 December 2014		Date of mailing of the international search report 24 FEB 2015
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