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Electrowetting Assisted Air Detrapping in Transfer Micromolding for Difficult-to-Mold Microstructures

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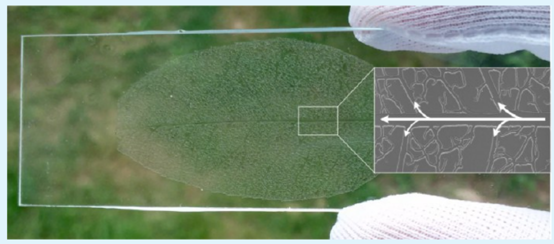
Supporting Information



ABSTRACT: As a widely applicable process for fabricating micro- or nanostructures, micromolding in atmosphere would require the removal or minimization of air-trapping in mold cavities so as to fill the liquid prepolymer fully into the mold for generating an exact polymer duplicate. This has been difficult, if not impossible, especially for a mold with high aspect ratio, varying size/shape, or isolated cavities because the air can be trapped inside such mold cavities in most variants of the molding process. This paper presents an electrowetting assisted transfer micromolding process to solve this problem. A feeding blade continuously supplies a UV-curable prepolymer over a dielectric-coated conductive mold placed on a progressively advancing stage. A voltage applied to the electrode pair composed of the feeding blade and mold generates an electrowetting of the prepolymer to the mold. The electrowetting allows for the three-phase contact line to pass progressively along the sidewalls and bottoms of the cavities, completely pushing out the air initially occupying the cavities, or generates an electrocapillary force large enough to pull the prepolymer deeply into the mold by compressing the air already trapped inside the cavities to a minimized volume. An experiment has been performed for micromolding with deep cavities of various shapes and sizes, demonstrating an essential improvement in the structural integrity of the polymer duplicates.

KEYWORDS: *microstructuring, molding process, electrowetting, high aspect ratio, UV-curable polymer*

1. INTRODUCTION

Micro/nanomolding has been considered as an approach for economically duplicating various functional structures, such as high aspect ratio micropillars for force sensing in microelectromechanical systems (MEMS),[1] pyramid microstructures of mesoporous TiO_2 for light-trapping in optoelectronics,[2,3] microchannels for guiding flow in microfluidics,[4,5] topography substrates for surface chemistry[6,7] or cell science and engineering,[8−10] etc. Obviously, the full filling of functional liquid-like (thermoplastic, UV- or thermocurable) materials into the cavities of a mold at atmospheric pressure would be highly desirable for the accuracy and yield of various molding processes, including micro/nanoimprinting[11,12] capillary force lithography,[13,14] micromolding in capillaries,[15−17] microtransfer molding (μTM),[18,19] and so forth, which were claimed to be of a nanoscale resolution. However, this has been difficult, if not impossible, especially for a mold structure with high aspect ratio, varying size/shape, or isolated cavities (deep microholes or isolated trenches, pockets of varying sizes, for instance), within which the air can inevitably be trapped during the molding process. To produce an exact duplicate from the mold in a mechanically driven imprinting process, for instance, a large pressure would be usually required to press the mold against the polymer-coated substrate to minimize the air volume already trapped in the mold cavities, and for a mold with deep microholes, the required pressure can possibly be so large as to result in an unacceptable deformation of the mold and duplicates.[11,12,20] Capillary force lithography requires no mechanical pressing force, yet at a cost of a long time for the trapped air to permeate through the gas-permeable soft mold (such as a mold of polydimethylsiloxane (PDMS)).[21,22] Micromolding in a capillary uses a capillary force to drive a liquid prepolymer laterally into the micro/nanochannels formed by the channel-carved mold in seamless contact with a substrate, but would be also time-consuming because of the viscous resistance of the liquid polymer and the lateral friction between the liquid and the channel walls, especially for long channels.[21−23] To improve the filling efficiency and effectively remove the air-trapping, researchers used a doctor blade to wade and drag an amount of liquid prepolymer passing over a soft mold in an attempt to allow the liquid to fill into the mold cavities (mostly shallow grooves or holes) along the sidewalls.[18−22,24] However, such an improvement can be discounted because of the difficulties in the removal of air trapped in the deep cavities of a mold that is treated for hydrophobicity, for easy demolding. Besides, a low Young's modulus of the soft mold used in these attempts is not well suitable for a structure with small and high aspect ratio features, because it tends to cause roof collapse, lateral collapse, or buckling of the duplicated features, as observed experimen-

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tally.[21,22,25,26] In summary, all these molding processes developed so far have been based on a strategy of either pressurizing the air already trapped inside the mold cavities to minimize its volume or having it permeate slowly through the molecule-level porous mold materials for an improved filling of the polymer into the mold cavities, yet demonstrating no proper capability of dealing with a difficult-to-mold structure, which is characteristic of such features as deep microholes or isolated trenches.

Obviously, for micro/nanomolding with a high geometrical fidelity, the use of a hard mold (a Si or SiO_2 mold, for instance) to sustain the structural integrity (i.e., with ignorable mechanical deformation) of the duplicates would be preferred. Yet, due to the air-impermeability and artificially hydrophobic property of the hard mold,[27,28] the air will not escape once being trapped in the deep mold cavities. Actually, whether an air bubble would be trapped or not in the mold's cavities mainly depends on the wettability of a mold surface, which has been investigated numerically and experimentally.[29−33] Hirai et al. and Reddy et al. numerically showed that a good wettability of the microcavities allows for more liquid to flow into them.[29,30] For instance, a mold made of a water-soluble polymer (poly(vinyl alcohol) or PVA), which has a good wettability for a kind of titania precursor solution, was well filled when the solution was spinned on the PVA mold.[33] On the contrary, for a mold with a dewetting or hydrophobic property, a certain volume of air tends to be trapped because the advancing three-phase contact line cannot continuously pass throughout the sidewall and bottom of a cavity before the liquid touches the next edge of the cavity.[31,32] Such an air-trapping phenomenon can be explained by the well-known Cassie-state dewetting.[34]

If a hydrophobic surface of a mold can be reversibly made hydrophilic during the filling process and recover to its initial low surface energy again before the demolding process, the filling would be easy, without causing a new problem in the subsequent demolding process, where the hydrophobic property of a mold is necessary. Our recent investigations suggested that the contact angle of a liquid UV-curable prepolymer dropped on a plane electrode coated with a dielectric layer (such as a SiO_2/Si substrate) was decreased by applying a voltage between the plane electrode and a needle electrode inserted into the liquid drop.[35,36] Such an electrically induced decline of the contact angle of a liquid on dielectric/conductor substrate is known as electrowetting on a dielectric (or EWOD).[37−42] The contact angle recovered to the initial value after the external voltage was switched off. Such reversible electrowetting of a liquid UV-curable prepolymer is desirable for both molding and demolding processes. In this paper, a microstructuring strategy based on electrowetting assisted transfer micromolding is proposed to properly fill the prepolymer into the mold cavities at atmospheric pressure, independent of their size or geometry.

2. EXPERIMENTAL DETAILS

The process of electrowetting assisted transfer micromolding is shown in Figure 1. The electrowetting of the UV-curable prepolymer to a conductive hard mold is generated by applying a voltage to an electrode pair composed of the mold and a feeding blade (Figure 1a). The blade is used to continuously supply the UV-curable prepolymer atop the mold placed on a horizontally moving stage. The electrowetting either allows for the three-phase contact line to pass throughout the entire mold surface (including sidewalls and bottoms of the cavities), completely pushing out the air initially occupying the cavities (see Figures S1 and S2 in the Supporting Information), or generates an electrocapillary force strong enough to pull the prepolymer deeply into the mold cavities, by compressing the air already trapped inside the cavities to a minimized volume. In either case, the prepolymer can be expected to fill the mold cavities with an essentially improved depth. Then a planar and transparent substrate is brought onto the prepolymer filled mold (Figure 1b), followed by UV flooding exposure through the substrate (Figure 1c). Demolding finally leads to a transfer of the polymer duplicate from the mold to the substrate (Figure 1d).

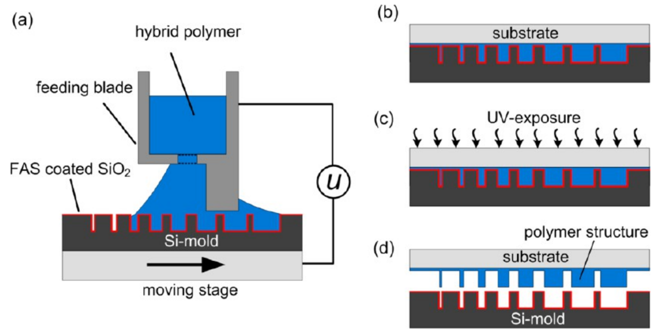

Figure 1. Illustrative experimental steps of electrowetting assisted transfer micromolding process. (a) A voltage is applied between the feeding blade and the mold on a moving stage to generate electrowetting to allow for a full filling of the UV-curable liquid prepolymer into the mold cavities; (b) a transparent substrate is brought into contact with the prepolymer filled mold; (c) the prepolymer is sandwiched between the substrate and the mold is cured by UV exposure; (d) the polymer duplicate is transferred onto the substrate after separating from the mold.

The voltage required to produce an adequate electrowetting depends on the distance of the feeding blade to the Si mold surface, which can be determined empirically or numerically.[35,36] In our experiment, a fixed and small distance of about 20 μm between the mold top and the lower edge of the feeding blade was selected to keep the required voltage at a manageable level (less than 1 kV_{pp}). A square-wave voltage with a proper potential and a frequency of 10 Hz was applied between the mold and the feeding blade (with V_{pp} standing for the amplitude from peek minus to peek plus in volts). The liquid prepolymer used in our experiment was an UV-curable acrylic-based component, available from Micro Resist Technology GmbH (with a commercial name Ormostamp).

3. RESULTS AND DISCUSSION

3.1. Improved Filling Efficiency by Electrowetting.

The filling efficiency for liquids into mold cavities can be improved by electrowetting, as shown in Figure 2. When no voltage is applied, a horizontal moving speed of 0.5 mm/s for the mold leads to a rather shallow filling into the cavities (Figure 2a), although a lower moving speed at 0.1 mm/s does increase the filling depth (Figure 2b). This is because the hydrophobic mold surface leads to a capillary force that is not strong enough to produce a fast prepolymer passing throughout the cavity sidewall and bottom to fully push out the air before the cavity top is capped. Therefore, only an extremely slow speed for the moving stage would lead to a complete filling of the cavities, which may be undesirable from a point of view of some mass applications. In comparison, when a voltage of 200 V_{pp} is applied, the mold cavities can be fully filled with the prepolymer even at the high moving speed of 0.5 mm/s (Figure 2c). This is because for the cavities well wetted due to the electrowetting, the liquid prepolymer tends to pass throughout the cavity surface (including its sidewall and bottom) so fast as to fully fill the cavity before the advancing front of the liquid reaches the next edge of the cavity (see

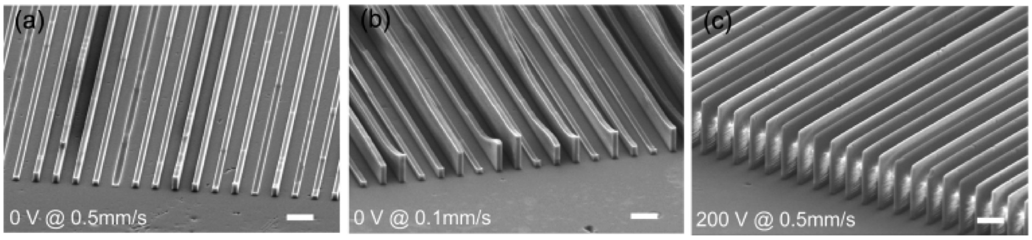

Figure 2. SEM images of grating structures duplicated from a high aspect ratio mold at different moving speeds of the stage and different voltages. (a) 0 V and 0.5 mm/s; (b) 0 V and 0.1 mm/s; (c) 200 V_{pp} and 0.5 mm/s. Scale bars: 20 μm.

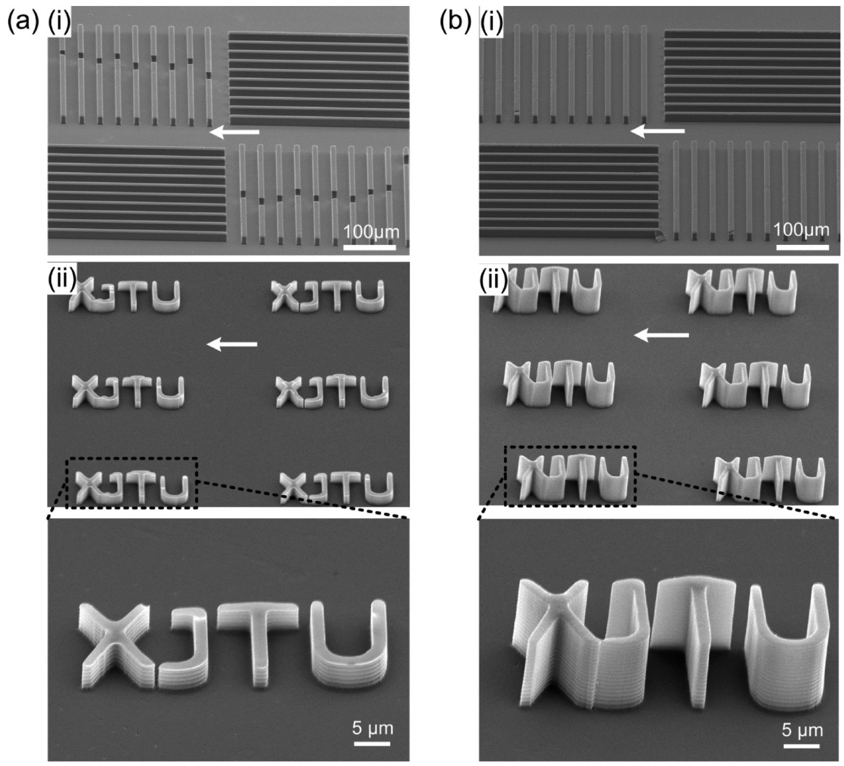

Figure 3. SEM images of a cross-grating structure and a complicated structure with letter cluster XJTU, fabricated with no voltage applied (column a) and with a voltage of 300 V_{pp} applied (column b). The arrows indicate the moving direction of the stage, and the moving speed was set as 0.05 mm/s when no voltage was applied and 0.5 mm/s when a voltage of 300 V_{pp} was applied.

Figures S1 and S2 in the Supporting Information). Expectedly, a higher voltage would allow for a higher moving speed of the stage, leading to a better molding rate.

3.2. Consistently Full Filling into Anisotropic Feature Assisted by Electrowetting. The electrowetting also allows for a consistently complete filling of prepolymer into cavities with varying shapes and geometrical irregularity (or anisotropy), as experimentally shown in Figure 3. The molding techniques proposed so far have been mostly used for fabricating shallow or regular structures. In the microtransfer molding[18,19] (or μTM, which is similar to the process proposed here, yet without electrowetting), for instance, the air-trapping could be minimized only when a blade was used to drag the liquid over a mold in a direction parallel to the microtrenches. This implies that such a microtransfer molding process can be effectively used for molding only parallel gratings of low aspect ratios with a proper fidelity to the mold. The fidelity of the duplicated structure from a mold with orthogonal gratings can become worse without the electowetting, as shown in Figure 3ai, where defects caused by the air-trapping in the duplicated gratings vertical to the blade moving direction can be observed. For a mold with more complex features (for example, a letter cluster "XJTU", which is an abbreviation for the authors' school), the micro air bubbles will be trapped randomly in the cavities, as shown in Figure 3aii. These results suggest that the filling process in a transfer molding without electrical actuation can be troublesome for a mold structure with anisotropically oriented features. In comparison, when a voltage of 300 V_{pp} is applied, all the trenches of the mold are completely filled with the prepolymer, leading to a defect-free polymer duplicate, as shown in Figure 3bi, and a mold with a smaller size and more complicated features can also be well filled, leading to a high fidelity in the polymer duplicate even with a high aspect ratio, as shown in Figure 3bii. These experimental results may well prove that electrowetting assisted transfer molding has an ability to consistently fill the liquid into mold cavities of complicated shapes, generating duplicates with an improved geometrical integrity and high aspect ratio.

3.3. Duplicate from a Mold with Features of Varying Size and Shape. Furthermore, the electrowetting in the transfer micromolding has an ability to generate an exact polymer duplicate from a mold with cavities of significantly

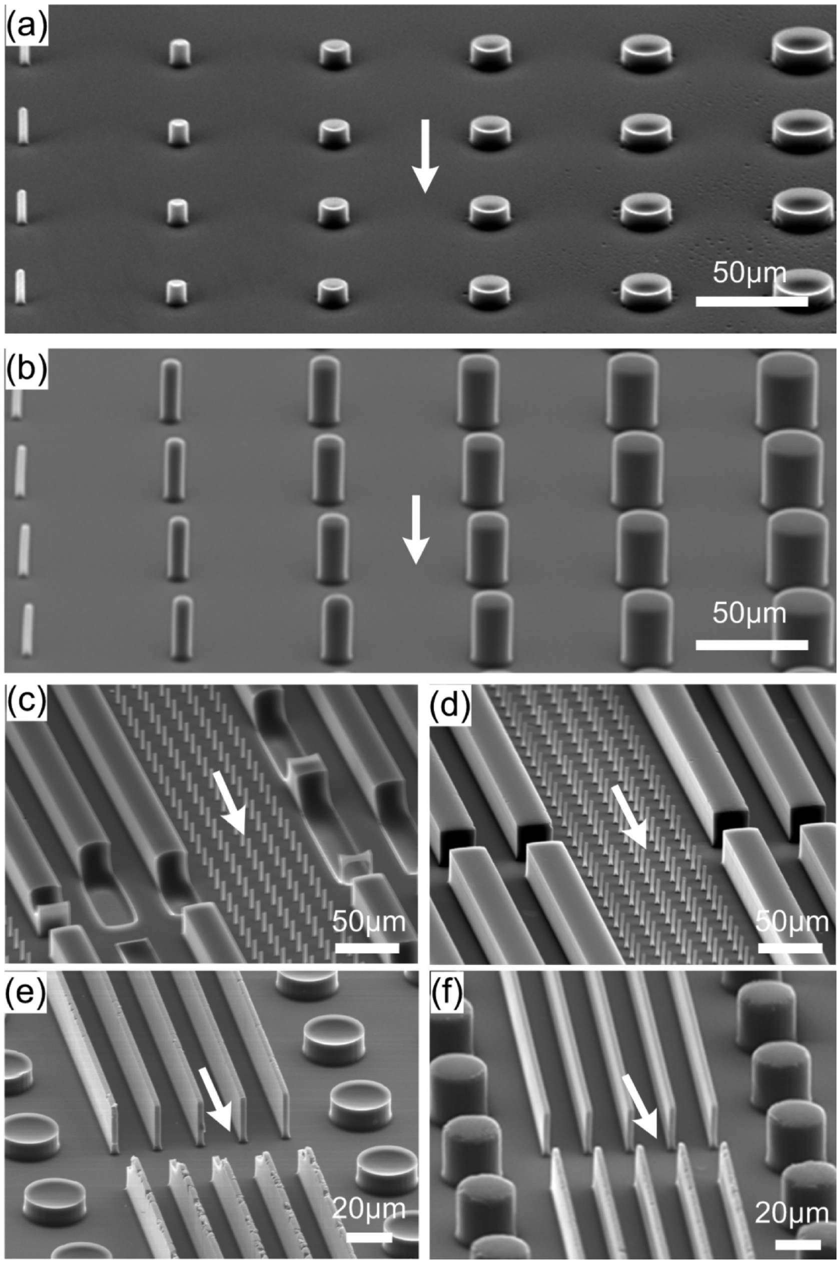

Figure 4. SEM images of polymer duplicates generated by applying a zero voltage (a, c, e) and a voltage of 700 V_{pp} (b, d, f), comparatively showing a structural integrity essentially improved by the electrowetting. The arrows indicate the moving direction of the stage at a speed of 0.5 mm/s. Note that the duplicated micropillars with different diameters have slightly different heights, due to a slightly uneven depth for the mold microholes of varying size, which can be caused by a microloading effect[44] typical during inductively coupled plasma (ICP) etching to the Si wafer in fabrication of the mold.

varying size and shape, as shown in Figure 4. It is interesting to note that the filling depth in a microhole (equal to the height of the duplicated micropillar) tends to decrease with the diameter of the microhole when no voltage is applied in the transfer micromolding, as shown in Figure 4a, suggesting that a smaller size of the feature allows for a deeper filling depth. This may be because the size-dependent capillary force, which increases with the decreasing microhole size, is dominantly driving the prepolymer in the microhole against the air pressure of the already trapped air.[35,43] The size dependence of the prepolymer filling in the mold cavities at a zero voltage can also been seen in Figure 4c,e, where large-size features (duplicated walls or pillars of larger size) tend to be generated with either defects or a shallow height. These results suggest that the transfer molding without electrowetting tends to generate a nonconsistent filling of the prepolymer in the mold with varying size features, which is undesirable from a molding accuracy point of view. In contrast, when a voltage of 700 V_{pp} is applied, all the microholes of varying size are properly filled, as shown in Figure 4b. The complete filling of the smaller holes is mainly accomplished by the electrocapillary effect (i.e., the decreased contact angle of the prepolymer in the holes leads to a larger capillary force to minimize the volume of the already trapped air).[35] The complete filling of the larger holes results from a continuous flow of the prepolymer along the sidewall and bottom of the holes to push out the occupying air completely. A well duplicated structure from a mold with a more complicated combination of varying shapes and sizes is

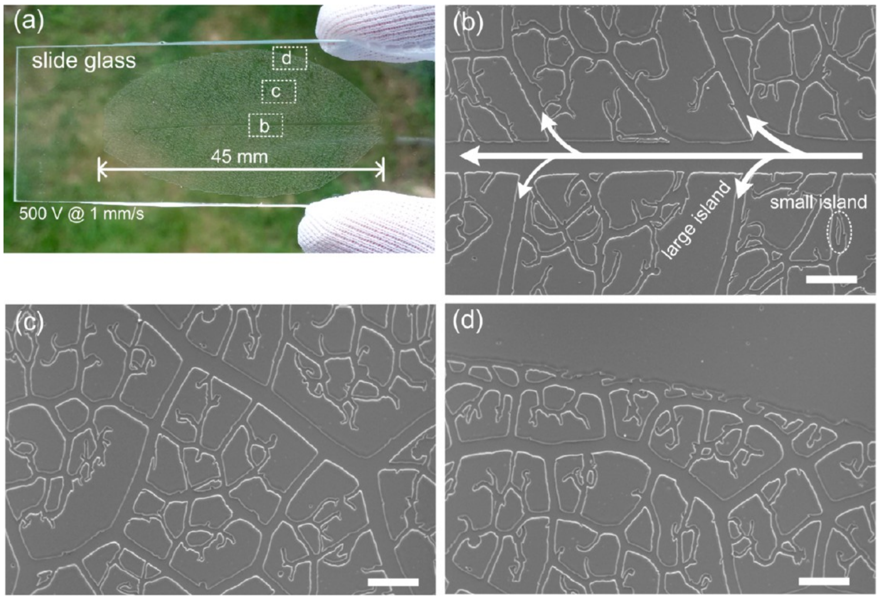

Figure 5. Microfluidic network mimicking leaf venation fabricated by electrowetting assisted transfer micromolding process. (a) Microfluidic network transferred on a slide glass; (b−d) zoomed SEM images of the microfluidics network at different positions as the dashed boxes indicated in panel a). The arrows in panel b indicate the naturally flowing direction of a liquid in the leaf venation. Scale bars: 500 μm.

shown in Figure 4d,f. These experimental results suggest that the strategy proposed may be well suitable for generating a high-fidelity duplicate from a mold with various complicated features, as shown by the three-dimensional (3D) and cross-section profiles of a Si-mold and its polymer duplicate in Figure S3 in the Supporting Information. Finally, the ability of the process for molding on a nanoscale was tested to a certain degree in our previous publication in producing a uniform nanopillar array over a small area by a prepolymer needle-dragging.[35]

Because complete filling of the prepolymer in the mold cavities is attributable to such electrohydrodynamic effects as electrocapillary force or electrowetting, as described above, a highest possible voltage can always be preferred as long as it does not cause an electrical breakdown to the liquid prepolymer or the dielectric coating on the mold (as discussed in Figure S4 in the Supporting Information). Because the blading and electrowetting progress horizontally, this process can be potentially implemented over a large area mold (see Figures S5 and S6 in the Supporting Information). Also, because the EWOD can happen to any conductive polymer or leaky dielectrics in a liquid form, the proposed approach can be expected to be applicable to a wide range of materials in practice (see Figures S7 and S8 in the Supporting Information).

3.4. Fabrication of Nature-Inspired Microfluidic Network of Leaf Venation. As a specific application, electrowetting assisted transfer micromolding has been finally tried to generate a microfluidic network mimicking leaf venation. Plant leaf venation commonly has convective microfluidic networks,[45−47] which can well homogeneously deliver water and nutrient contents for the tissues of a leaf. The unique properties of these microfluidic networks in nature inspired numerous biomimetic structures that have shown great promise for applications in chaotic mixing, self-healing materials, and tissue engineering.[48−50]

The process for fabricating a Si-mold with a network mimicking leaf venation is described in detail in the Supporting Information. By using such a mold, a polymer microfluidic network mimicking the mulberry leaf venation was fabricated via the molding process proposed, as shown in Figure 5, demonstrating well duplicated islands with a size that spatially varies significantly.

4. CONCLUSION

In summary, this paper has proposed a polymer microstructuring approach by electrowetting assisted transfer micromolding that has the ability to solve the problem with a poor structural integrity of the polymer duplicate generated from a mold that contains such difficult-to-mold features as high aspect ratio, varying-size/shape or isolated cavities, etc. The approach is based on a strategy of filling the prepolymer into the mold cavities to the highest possible extent. Then either the electrowetting drives the three-phase contact line so as to pass progressively throughout the entire mold surface (including sidewalls and bottoms of the cavities), completely pushing out the air initially occupying the cavities (in the case of larger size cavities), or the electrocapillary force due to the electrowetting becomes large enough to pull the prepolymer deeply into the mold, compressing the air already trapped inside the cavities to a minimized volume (in the case of smaller size cavities). The testing results for molding with some typical structure features have suggested the versatility of the proposed approach.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Illustration and experimental observations of the wettability-dependent filling, the cross profiles of a Si-mold and the corresponding polymer duplicate, large area polymer duplicates using electrowetting assisted micromolding process, voltage-dependent fidelity of the polymer duplicates, electrowetting and microstructuring of HEMA and PEG-DA, the process for fabrication and surface treatment of Si-mold, and a description of materials and equipment. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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