Manipulation of Liquid Filaments on Photoresponsive Microwrinkles

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Ⓢ *Supporting Information*
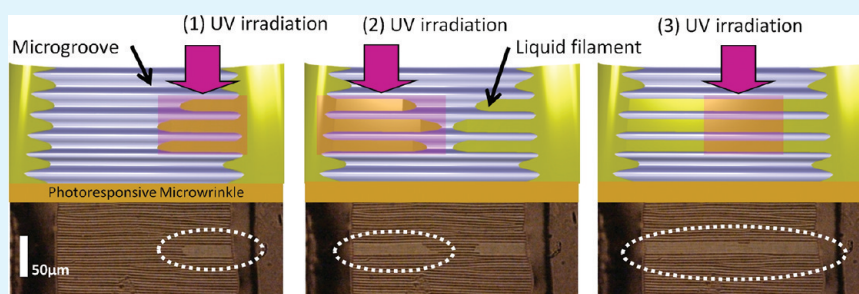
ABSTRACT: Microwrinkle grooves serve as open microchannel capillaries, where the capillary action depends on the wettability of a liquid on the groove surface. Here, we report the photoinduced capillary action of a liquid in such microwrinkle grooves. The wettability is changed through the irradiation of a photoresponsive microwrinkle surface. By utilizing micropattern light-projection apparatus, we prepare liquid filaments that fill only the microgrooves prescribed by the patterned light, with micrometer-scale spatial resolution. This new technology enables the precise spatial control of liquids on a solid surface, and thus, is applicable in the fields of micropatterning and open-channel microfluidics.

KEYWORDS: microwrinkle, liquid manipulation, microfluidics, photoresponsive polymer, wettability control

■ INTRODUCTION

The capability to control liquid motion on small length scales is important in the fields of micropatterning,[1] microfluidics,[2,3] biosensing,[4] and printed electronics.[5] Recently, we reported a simple method for transforming liquid morphology on the micrometer scale or smaller by using dynamically shape-tunable microwrinkles.[6,7] When a hard layer supported by a soft substrate is compressed laterally beyond a critical strain, buckling of the hard layer occurs, leading to the formation of sinusoidal surface undulations (wrinkles) with a characteristic spatial wavelength Λ.[8−10] The microgrooves of these microwrinkles can serve as open microchannel capillaries, where only the grooves are filled with liquid; the crest parts remain exposed to the air. Liquid stabilized in a straight groove is called a liquid filament (LF). For the formation of LFs, the groove morphology and surface wettability are critical properties.[6] By changing the morphology, LF formation can be controlled via capillary action,[6] and can be further transformed into small droplets by changing the groove direction.[7] However, the wettability was fixed in previous experiments. If the wettability is enhanced in response to an external stimulus, capillary action would be triggered without any change in the morphology of the microgrooves.

One way to switch the surface wettability is to exploit the reversible photoisomerization of azobenzene moieties.[11−19] Azobenzene moieties have received much attention because of their ease of chemical modification and their photoinduced

structural change between the cis and trans forms. This transformation can change the interfacial properties, and thus, the wetting properties. As a result, it becomes possible to manipulate liquid droplets on flat solid surfaces possessing azobenzene chromophores,[12,14,17] where the macroscopic motion of liquids is induced by ultraviolet (UV) and visible (vis) light irradiation. This photoinduced switching of the wettability may be applicable to triggering the capillary action of liquids in microwrinkle grooves. In particular, it is expected that the precise spatial control of this capillary action could be achieved by patterned light irradiation,[20−23] which would be a great advantage for practical applications.

Herein, we report a new technique using photoresponsive microwrinkles to prepare micrometer-scale liquid filaments. The wetting characteristics of the microwrinkle surface, which is coated with a photoresponsive polymer, are switched by the light-induced photoisomerization of azobenzene moieties incorporated in the polymer. The capillary action of a liquid in the microgrooves is triggered by the contact angle being lowered because of the photoisomerization. Using micropattern light-projection apparatus,[20] we fabricate liquid filaments in the desired microgrooves of microwrinkles. This aspect represents a sharp contrast with the previous method, in which spatial
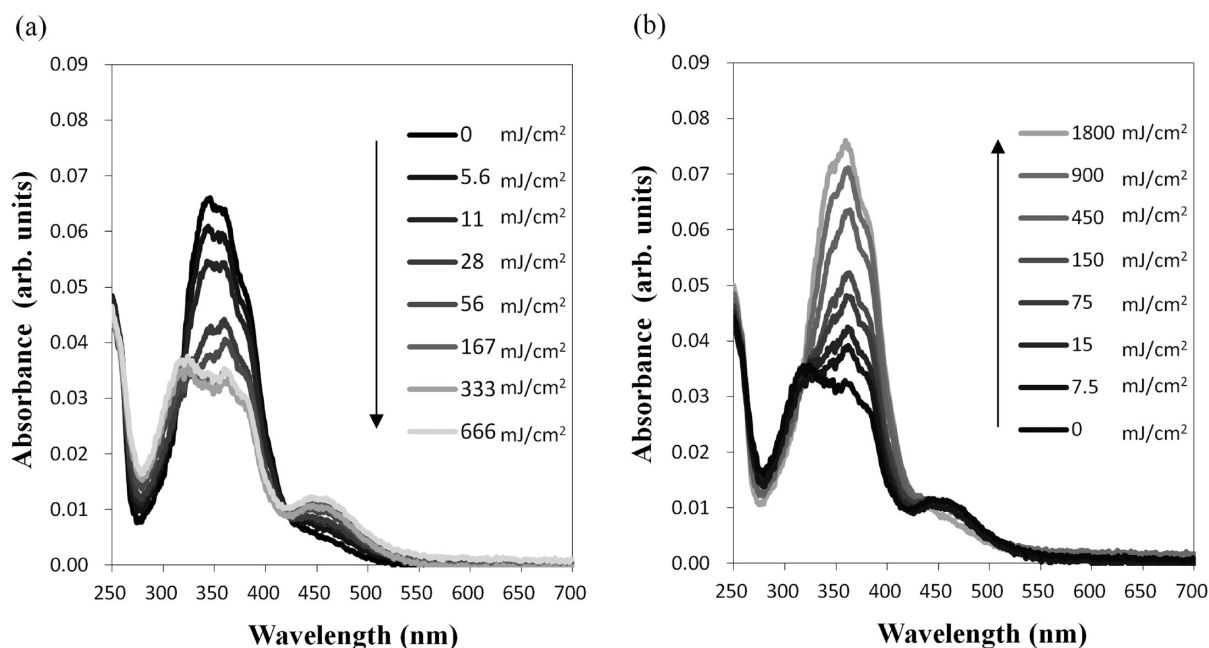
Figure 1. UV−vis spectral changes of azobenzene polymer on polyimide-coated glass substrate upon light irradiation at wavelengths of (a) 365 nm and (b) >420 nm with different light energies.

control of LF formation was hampered by the technical difficulties associated with local control of the applied strain.[6,7]

EXPERIMENTAL SECTION

Materials. A monomer containing an azobenzene unit, 6-[4-(4-ethoxyphenylazo)phenoxy]hexyl methacrylate, was synthesized according to the literature procedure.[24] Poly{6-[4-(4-ethoxyphenylazo)-phenoxy]hexyl methacrylate]} (2Az6) was synthesized by atom-transfer radical polymerization according to the literature procedure.[25] Anisole, which is the solvent used for solution polymerization, was purified by distillation from sodium and benzophenone. CuCl (Kanto Chemical), which was used as a catalyst, was washed successively with acetic acid and diethyl ether, then dried, and stored under nitrogen. 2-Bromo-2-methylpropionyl chloride, 11-bromo-1-undecanol, 4-butylaniline, methacrylic acid, and dicyclohexylcarbodiimide were purchased from Kanto Chemical and used without further purification. The ligand 1,1,4,7,10,10-hexamethyltriethylenetetramine (Aldrich) was used as received, without further purification. Propylene carbonate (PC) and poly(pyromellitic dianhydride-co-4,4′-oxydianiline) (PAA) were purchased form Aldrich and used without further purification. The yellow 2Az6 polymer was collected by reprecipitation from methanol. From gel permeation chromatography (GPC) measurements, $M_n = 4800$ and $M_w/M_n = 1.28$.

Preparation of Photoresponsive Microwrinkles. Microwrinkles with aligned grooves were prepared according to the methods described in our previous reports (see Figure S1 in the Supporting Information).[6,7] An N-methylpyrrolidone (Aldrich) solution of PAA was spin-coated (5000 rpm) onto a smooth surface of polydimethylsiloxane (PDMS) elastomer (12 mm × 12 mm × 5 mm, Sylgard 184, Toray-Dow) and heated to generate a polyimide (PI) film on the surface. During heating at 180 °C, the sample was compressed uniaxially to a strain of approximately 5%, so that the sample expanded anisotropically in the direction perpendicular to the compression during curing. Thus, a hard PI surface film was formed on an anisotropically expanded PDMS substrate. Upon cooling to 25 °C and release of the applied strain, aligned microwrinkles were formed in the groove direction parallel with the compressed direction because of the buckling of the hard PI film supported by the soft elastic PDMS substrate. The wavelength Λ was controlled by adjusting the initial concentration of the spin-coated solution (1.3 wt %) for Λ = 3.3 μm. The photoisomerizable polymer 2Az6 was spin-coated (2000 rpm)

onto the wrinkle surface of the PI/PDMS sample to prepare the photoresponsive microwrinkle surface. Before each spin-coating process, the surface was weakly treated with Ar plasma (SEDE-P, Meiwa Forsis) to enhance the wettability of each polymer solution. The microwrinkles had a typical aspect ratio R of 0.15 ± 0.02, where R = A/Λ and A is the wrinkle depth observed by atomic force microscopy (see Figure S2 in the Supporting Information). For the UV−vis spectra and contact-angle measurements, glass coverslips were used as substrates instead of the PDMS elastomer.

Micropattern Light-Projection Apparatus. For the irradiation of the surface with patterns on the micrometer scale, we used micropattern light-projection apparatus that comprised a DESM-01 computer-controllable maskless micropattern projection unit (Engineering System), a CCD camera (Sigma Koki), and an inverted optical microscope (IX-71, Olympus).[20] This projection unit, consisting of micro mirror devices, was connected to a dual-lamp housing attachment (U-DULHA, Olympus) with UV and vis light-emitting diodes (LEDs; M365L2 and MCWHL2, Thorlabs). Although this apparatus would allow us to control the brightness and shape of the pattern arbitrarily, we used simple rectangular patterns in this study. The optical microscopy images were acquired with a commercially available video camera (CX-12, Sony) (see Figure S3 in the Supporting Information). The intensity of UV light illumination, measured with an optical power meter (3664, Hioki), was 26.0 mW/cm² from the UV LED (365 nm) via the objective lens (SMPlan 50×, Olympus).

Physical Properties. The UV−vis absorption spectrum of the polymer with azobenzene units was measured using a UV−vis spectrophotometer (U-3100, Shimadzu). GPC was conducted on a Shimadzu system comprising an LC-10ADvp pump unit, an SPD-10Avp UV detector, a CTO-10Avp column oven, and an SCL-10Avp controller. The molecular weights of the polymers were determined with reference to polystyrene standards in tetrahydrofuran solution. The static contact angle was measured using a standard contact-angle meter (Drop Master 300, Kyowa Interface Science) in air at 25 °C.

RESULTS AND DISCUSSION

Photoisomerization of 2Az6. First, we investigate the photoisomerization of 2Az6 spin-coated on the glass substrate by measuring the UV−vis spectra upon irradiation with UV and vis light. As the irradiation energy of UV light at 365 nm

increases (Figure 1a), the absorption intensity of the $\pi-\pi^*$ transition band at 360 nm decreases, and that of the $n-\pi^*$ transition band at 450 nm increases. This indicates that the *trans* isomer changes to the *cis* one. Then, the *cis* isomer is exposed to vis light with a wavelength larger than 420 nm at various irradiation energies (Figure 1b). The spectral changes indicate the reverse photoisomerization, i.e., the change from the *cis* to the *trans* isomer. The present results indicate that the reversible photoisomerization[26,27] of 2Az6 occurs in the thin-film form. In addition to the spectral changes due to the alternation of the molecular structure, the dipole moment of the molecule also changes, with the *cis*-azobenzene having a higher dipole moment. Thus, the surface of the UV-exposed 2Az6 polymer terminated with *cis*-azobenzene is expected to show a higher surface free energy, and hence, a lower contact angle for certain liquids,[28] as will be described later.

Condition for LF Formation through a Change in Wettability. We have studied the general condition for inducing capillary action in microwrinkle grooves.[6] Figure 2
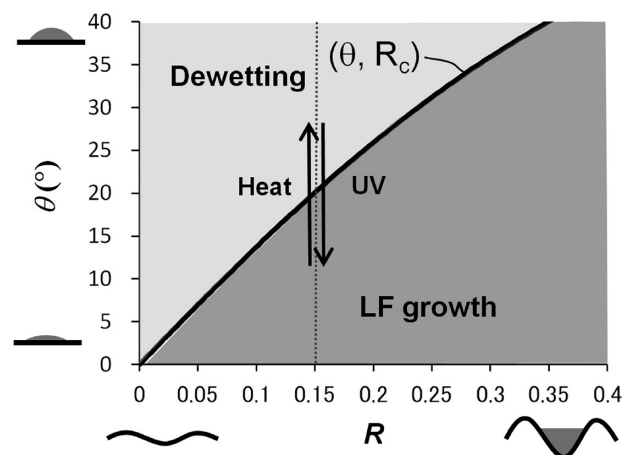

Figure 2. Theoretical analysis of LF formation. Diagram of LF formation with respect to the equilibrium contact angle, θ, and the aspect ratio, R, from the theoretical calculations in ref 6.

shows a theoretically calculated diagram of LF formation from a reservoir on microgrooves with respect to θ (the equilibrium contact angle between a liquid and a surface without wrinkles) and R (the aspect ratio).[6] LFs grow because of the capillary action in a microwrinkle if θ and R are in the lower right region compared to the critical line in Figure 2. On the other hand, in the upper left region in Figure 2, where θ is relatively higher and R is lower, no LFs grow. When the contact angle is lowered by photoirradiation, LF formation is triggered at a fixed R value of a microwrinkle. This process is indicated in the diagram by the vertical arrow (Figure 2). On the present microwrinkles with $R = 0.15$, the capillary action of the liquid to form LFs in the microgrooves is triggered when $\theta < 20°$.

Photoinduced Change in Contact Angle. We examined the θ values of three liquids on a flat surface at room temperature to eliminate the effect of the microstructure on the macroscopic contact angle (Table 1). The θ values of propylene carbonate (PC),[29] oleic acid, and 4-cyano-4′-pentylbiphenyl (5CB) on PI with and without the 2Az6 polymer layer were measured before (*trans*-rich) and after (*cis*-rich) irradiation with UV light. After UV irradiation, the θ values on the *cis* isomer indeed decreased because of an increase in the polymer dipole moment; the surface wettability on 2Az6 was enhanced by UV

Table 1. Contact Angles (θ) of Various Liquids on 2Az6 and PI Surfaces

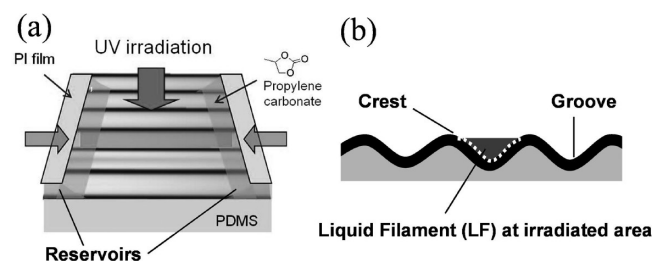| liquid[a]	contact angle θ (deg)		
	trans-rich	*cis*-rich	PI
propylene carbonate (PC)	43	11[b]	19
Oleic acid	23	5	17[c]
5CB	28	15	15[c]

[a]Values are within an experimental error of ±2, except for PC on *cis*-rich 2Az6. [b]Contact-angle value is within an experimental error of +8/−4. [c]Data from ref 6.

irradiation. With this change in θ, the formation of LFs on the microwrinkles can be triggered by photoirradiation, because θ crosses the critical line (Figure 2) dividing the states of LF growth and dewetting.

We also measured the contact angle of PC on the film after vis light irradiation on the *cis*-rich state. Although the spectral change after vis light irradiation (Figure 1b) indicated that the *cis* isomer was transformed back to the *trans* one, the θ value increased only slightly to $18 \pm 2°$ even after irradiation with a dose of 750 mJ/cm² for 50 min. Thus, for the present system, it is difficult to induce the dewetting state from the LF growth state by photoirradiation. However, after seven days at room temperature, the original θ value of 49° for the *trans*-rich film was recovered for the vis-irradiated film. The results suggest that certain changes in the polymer configuration associated with the two photoisomerization processes differ kinetically, i.e., a slow relaxation process takes place in the polymer after vis irradiation. Although the mechanism is unclear here, the reversibility of the change in contact angle is confirmed in principle. For practical applications, this slow process should be minimized by optimizing the photoresponsive surface materials; this will be considered in a future study. Because of such technical limitations, only the UV-induced decrease in contact angle was utilized to form the LFs in the following experiments.

Spatially Controlled Formation of Liquid Filaments by Patterned Light Irradiation. Scheme 1 shows our strategy for forming a channel of LFs on microwrinkles. First, a small amount (0.5 μL) of liquid is placed on the photoresponsive microwrinkles, and a PI film (2 mm × 4.5 mm, 25 μm in thickness; Kapton, Toray-Dupont) is placed on this liquid to form a liquid reservoir with a straight three-phase line of liquid/

Scheme 1. Schematic Diagrams of Photomanipulation of LFs in Photoresponsive Microwrinkles: (a) Birds-Eye-View Image of the Experimental Procedure;[a] (b) Cross-Sectional Image of the Microgrooves[b]

[a]A rectangular area including the liquid/solid/air interface is irradiated by UV light.

[b]Formation of LFs within the microwrinkle grooves due to the lowered contact angle occurs only in the UV-irradiated region.
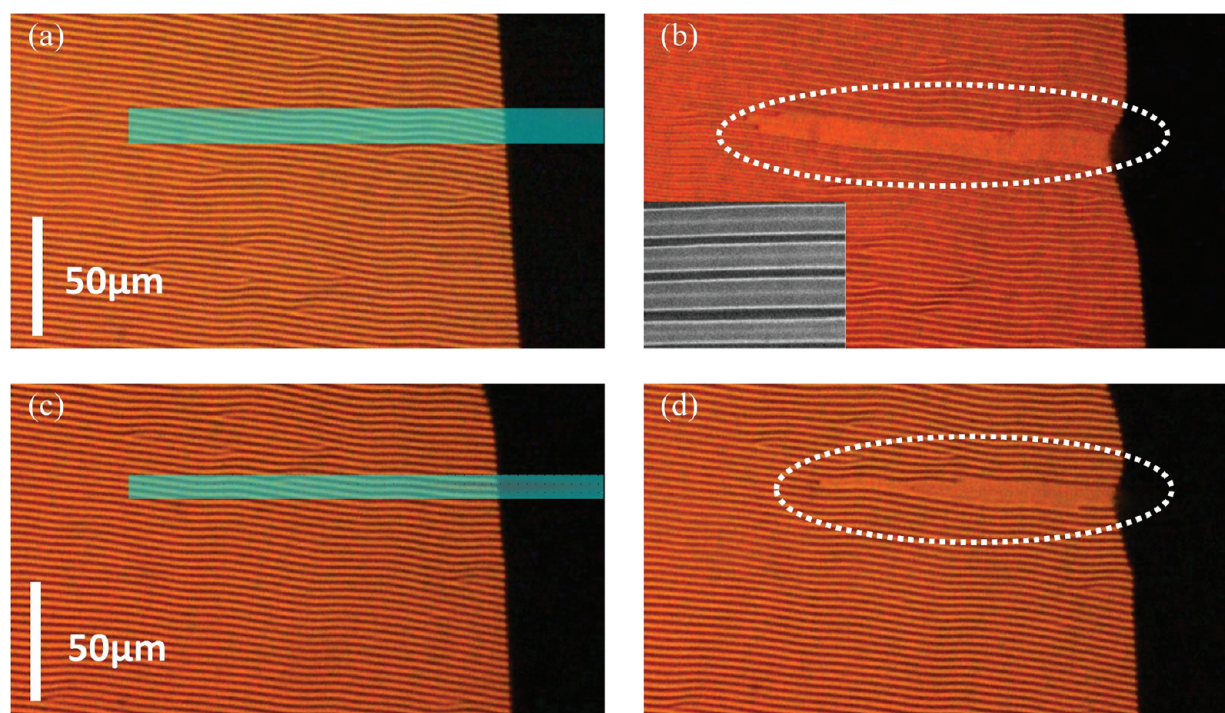
Figure 3. Optical microphotographs of photoresponsive microwrinkles. The rectangular UV-irradiated areas with widths of (a) 15 and (c) 10 μm indicated schematically by the light blue areas. Resulting LF formation after UV light irradiation, where the widths of the irradiated areas are (b) 15 μm and (d) 10 μm (white dotted circle). Inset in b shows a magnified optical image of the LFs (19 μm × 14 μm). Note that the narrow, dark stripes are crests, and are not covered by the liquid.

solid/air. This three-phase line is set normal to the groove direction. To make a connection between the LFs, two reservoirs are prepared in parallel on the microwrinkles across the grooves. Next, a rectangular area on the microwrinkle surface is irradiated with UV light using the micropattern light-projection apparatus.[20] In this UV-irradiated area, the θ value of the liquid decreases to trigger the capillary action, leading to the formation of LFs.

Figure 3 shows microphotographs of the LFs on the microwrinkles coated with 2Az6, which were taken with an O-54 sharp-cut filter (Hoya) that cuts light below 540 nm. This filter was used to prevent the *cis–trans* photoisomerization of azobenzene that results in a slight increase in contact angle. The rectangular part (width: 15 μm; length: 200 μm) shown in Figure 3a was exposed to light irradiation. Upon UV irradiation for approximately 20 s, LFs grow from the liquid reservoir (see the Supporting Information, Movie S1). We note that LFs appear only in the area of UV irradiation (Figure 3b), and that each LF is confined within each groove, with the crest parts remaining exposed to the air (Figure 3b, inset). We can further reduce the width of the irradiated area to 10 μm, and thus, control the number of derived LFs (Figure 3c,d). With the present experimental setup and wrinkle wavelength of 3.3 μm, it is possible to induce the formation of as few as three LFs. Furthermore, when a wrinkle wavelength larger than 10 μm is used under the present irradiation conditions, it is possible to induce an LF within a single groove at a desired position.

Figure 4 shows an example process for the formation of a connection between LFs at a desired position. First, UV irradiation of a rectangular area triggers the capillary action of liquids from the liquid reservoir on the right side; Figure 4b shows the resultant LF formation from this reservoir. Then, the same procedure is applied to the microwrinkles on the left side,

and finally, the remaining intermediate grooves are irradiated by UV light. As a result, the LFs drawn from the right and left liquid reservoirs are connected. As shown in Figure 4, the connected LFs were formed in only four microwrinkle grooves (see the Supporting Information, Movie S2). This procedure enables the directed mixing of two liquids in each microgroove with a width of approximately 3 μm through time-dependent mutual diffusion. The present results demonstrate the spatially controlled formation of LFs by patterned photoirradiation on a micrometer scale.

■ CONCLUSIONS

We have shown that liquids on microwrinkle grooves coated with a photoresponsive polymer can be manipulated on the micrometer scale by patterned photoirradiation. The wetting characteristics of the microwrinkle grooves were switched by photoisomerization of the azobenzene units incorporated in the polymer. The use of light as an external stimulus is advantageous for the fine spatial and sequential control of LF formation. For this purpose, micropattern light-projection apparatus was used. It was demonstrated that liquids were drawn precisely from a liquid reservoir through the activated capillary action. A connection between two liquid reservoirs was also made through the spatially controlled formation of LFs. These processes provide basic procedures for precise liquid micromanipulation based on microwrinkle technology.[30] No external pumping system is needed for this technique, so it may be possible to propose a new design for microfluidic channels without pumps and valves. Although the light-driven receding process of the LFs, as opposed to their formation, is not shown here, a photoresponsive microwrinkle and a liquid with lower contact-angle hysteresis would be suitable for this. In principle, the present open microfluidic system can be
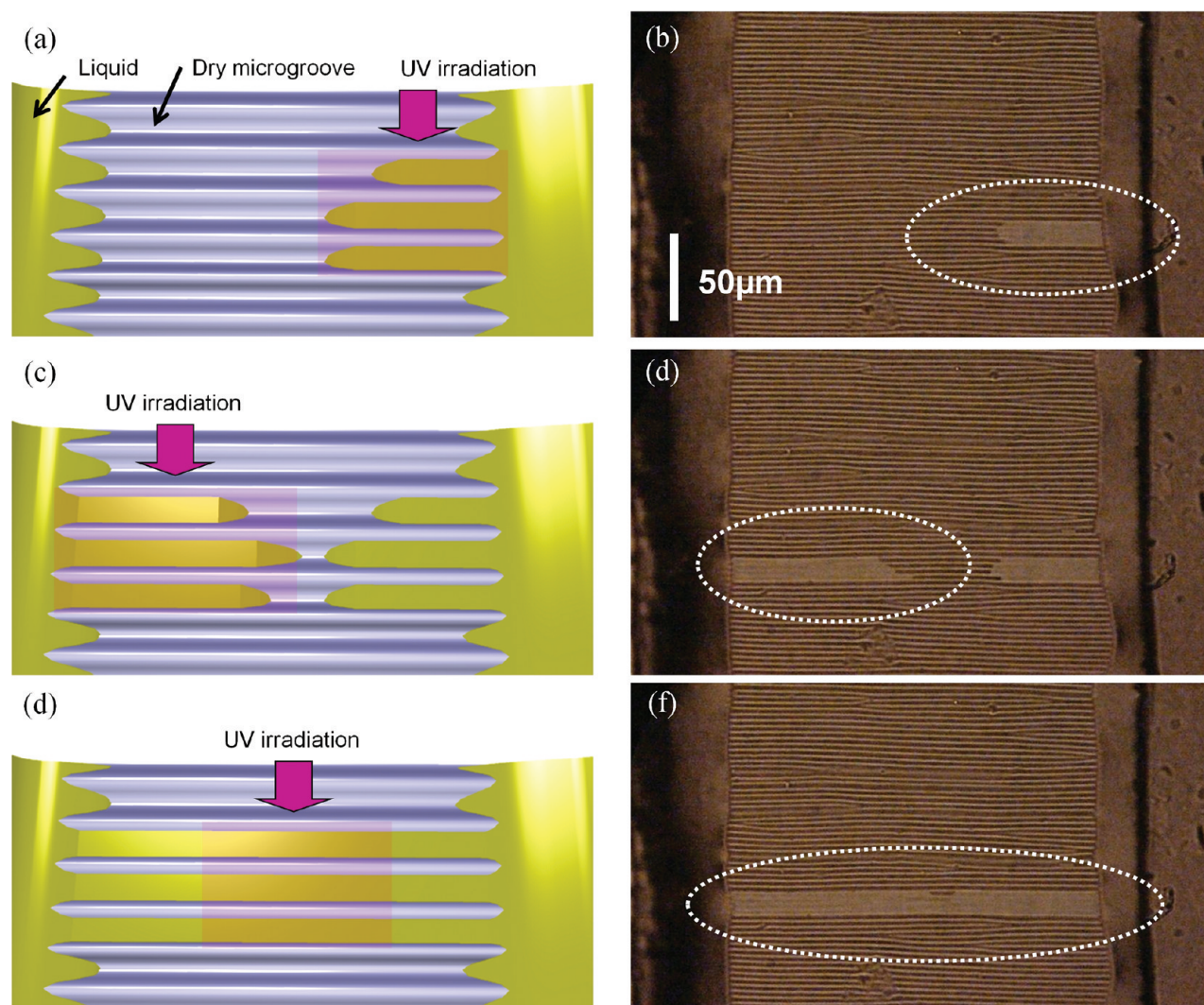
Figure 4. (a, c, e) Schematic birds-eye-view images of sequential UV irradiation with a rectangular pattern at different positions. (b, d, f) Optical microphotographs of photomanipulation of LFs on photoresponsive microwrinkles with an irradiated area of width 15 μm. Corresponding LF formation after each UV irradiation indicated in a, c, and e, respectively. Two sets of LFs drawn from each side are connected in the image in f. Note that the liquids are present only in the grooves; the crest parts remain exposed to the air.

applied to any liquid. If we could prepare photoresponsive surface materials with appropriate changes in the contact angle for water, for instance, with θ varying from 30 to 10° at R = 0.15, we could use the system with aqueous solutions. However, a chamber would be required for liquids with high vapor pressures to suppress drying, especially on small scales. Nevertheless, the open microfluidic system is advantageous for the application of local stimuli to liquids, because the liquids can be accessed directly; for example, chemicals or colloids could be deposited from the top. Therefore, the present light-induced formation of LFs on microwrinkles will open up new possibilities for applications in microfluidics, including lab-on-a-chip technology, nanosynthesis, and micropatterning.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Schematic diagram of the preparation of photoresponsive microwrinkles (Figure S1), atomic force microscopy images and cross-sections of the microwrinkles with and without the photoresponsive polymer on a PI/PDMS substrate (Figure S2), and a schematic representation of an inverted optical microscope with the micropattern light-projection apparatus (Figure S3) (PDF); movies showing LF formation through UV irradiation on microwrinkles (Movies S1 and S2). 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.

■ ACKNOWLEDGMENTS

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(29) Ideally, propylene carbonate (PC) and 2Az6 should be immiscible in each other, because such an irreversible process is unfavorable for the stable control of wettability. In the present system, slight dissolution of 2Az6 into PC might occur. However, the main objective here is to demonstrate that the photoinduced change in the contact angle can trigger capillary action in the microwrinkle grooves. Therefore, although the optimization of the photoresponsive surface materials is critical for practical applications, this aspect is left for future study.

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