Inkjet-Printed Monolayers as Platforms for Tethered Polymers

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Combining inkjet printing and atom-transfer radical polymerization (ATRP) provides a straightforward and versatile method for producing patterned polymer surfaces that may serve as platforms for a variety of applications. We report the use of drop-on-demand technology to print binary chemical gradients and simple patterns onto solid substrates and, by using surface-confined ATRP, amplify these patterns and gradients. Chemically graded monolayers prepared by inkjet printing dodecanethiol and backfilling with 11-mercaptoundecanol showed continuous changes in the water contact angle along the gradient. These samples also exhibited a distinct change in the intensity of methyl group and C−O stretching modes along the gradient. Graded or patterned polymer layers were produced by growing, with ATRP, tethered poly(methyl methacrylate) (PMMA) layers from gradient or patterned printed monolayers that contained a bromo-capped initiator. Atomic force microscopy and optical microscopy confirmed that the PMMA layers amplified the underlying printed initiator layer with remarkable fidelity.

Introduction

Inkjet printing, a technique that creates and releases droplets of fluid on demand and precisely deposits those droplets on a surface, has received increased attention for its novelty and ability to produce patterned and templated material structures. Although inkjet printing is widely used for home and office printing, its use in nongraphic applications has gained importance lately because it allows for high-throughput manufacture of "printed" materials, can be fully automated and computer controlled, and enables flexibility in creating designs. In materials fabrication applications,[1−5] inkjetting offers the advantages of contactless printing and eliminates the use of a die or photomask, thus allowing modification of the pattern quickly and effortlessly without having to produce a new "master" or die.

Drop-on-demand (DOD) inkjet printers use printhead nozzles that each eject a single drop of ink only when activated. Thermal and piezoelectric inkjets are the two most common DOD technologies. Inkjet printers eject small drops of ink through nozzles placing them precisely on a surface to form contrasting regions of lines, curves, and shapes that we interpret as text or images. These small drops typically have volumes on the order of picoliters. Many of these drops make up the tiny features known as pixels, which when arranged collectively on the surface in a specific style makes the design or pattern. Hence, while the feature resolution describes the distance between two adjacently placed ink drops, it is the dissimilarity between printed pixels that defines the pattern resolution, which defines the ability of the printer to make distinguishable visual graphics. The advantages of inkjet printing include small drop volumes, high printhead operating frequency, excellent system reliability, and highly controlled ink drop placement.[6] Variation in the printer resolution affects the quality and sharpness of the printed image or patterns. The soft lithography techniques, viz., microcontact printing, replica molding, and micromolding in capillaries, can achieve resolutions on the order of few nanometers.[7] However, these lithographic techniques suffer from the lack of a direct automation process. DOD technology coupled with a high-resolution printer could achieve a similar level of resolution, and the process could be automated using simple computer software programs, which would eliminate the use of masks or dies for patterning.

In this article, we report the use of inkjet printing for developing patterned and gradient soft surfaces. Although DOD has been used previously for cell printing[1] and printing of particulate suspensions,[2] light-emitting polymer displays,[3] polymer thin-film transistor circuits,[4] and biochips,[5] its use in concert with atom-transfer radical polymerization (ATRP) or with any other controlled polymerization method to afford a simple technique to produce 3-dimensional (3D) soft surfaces has not been reported. Forming 3D structures requires control over the lateral and vertical dimensions. The lateral arrangement can be controlled by accurately placing the printed components on the surface, and the layer thicknesses (vertical dimension) of the surface-tethered polymers can be manipulated to achieve the desired 3D structures.

In this scheme, designs are developed on the surface by precise placement of thiol-terminated ATRP initiator molecules, also known as polymerization initiation molecules (PIMs), using an inkjet printer. ATRP is used for surface-confined polymerization to produce the anchored polymer layers on surfaces. The PIM initiates polymerization by generating radicals that can open double bonds of monomers and consequently grow polymer chains from the substrate.[8] The discovery of transition metal-catalyzed

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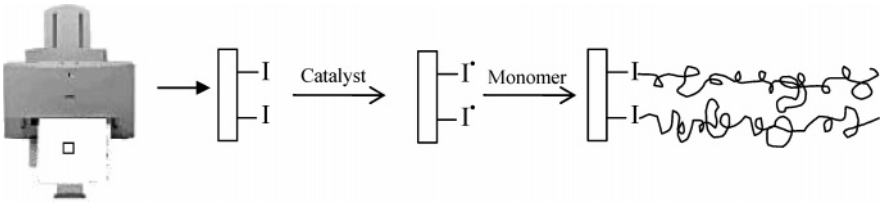

Figure 1. Schematic of the process to produce surface-tethered polymer layers by inkjet printing of initiator molecules and surface-confined ATRP.

living radical polymerization, developed independently by Matyjaszewski and co-workers[9] and Sawamato and co-workers,[10] has led to polymerization methods that produce surface-tethered polymers of controlled molecular weights and narrow molecular weight distributions.

Since its discovery, ATRP has been used to polymerize a wide variety of monomers, including acrylates, styrenes, and acrylonitriles.[11] ATRP is tolerant to many monomer functionalities because of its radical nature. In the present study, we use surface-confined ATRP to produce tethered layers of poly(methyl methacrylate) (PMMA). As outlined earlier, the process used to create the surface-tethered polymer layer on model gold surfaces involves multiple steps, which are depicted in Figure 1.

Experimental Section

Preparations. Gold-deposited silicon substrates were used in our studies. A 1000 Å gold layer was sputter-coated onto 10 mm × 25 mm silicon wafer chips that had been previously coated with a 100 Å binder layer of chromium. Gold surfaces were cleaned just prior to use using a Boekel ozonation chamber for 4 min. The PIM ($BrC(CH_3)_2COO(CH_2)_{11}S)_2$ was synthesized using a literature procedure described by Shah et al.[12] where 2-bromoisobutyryl bromide was reacted onto a disulfide material to form the bromocapper PIM. Inkjet printing was used to print this PIM directly onto the gold substrate as gradients or patterns for ATRP. The monolayer-modified gold surfaces were washed with ethanol and dried with a stream of nitrogen prior to characterization experiments. Standard surface characterization techniques such as Fourier transform infrared-external reflection spectroscopy (FTIR-ER), static water contact angle, optical microscopy, and atomic-force microscopy (AFM) were used to study the structure and properties of the modified surfaces.

Printing Solutions. Solutions (1.5 mM) of dodecanethiol and 11-mercaptoundecanol (MUT) were prepared in anhydrous ethanol for printing. A 1 mM solution of the bromo-initiator in anhydrous ethanol was prepared under a continuous nitrogen purge. Differences in the hydrophilicity of monolayers made from CH_3-capped dodecanethiol and OH-capped MUT allow for easy characterization of printed monolayers. In monolayers printed for polymerization, the CH_3-capped species serves as a "spacer" that helps ensure formation of a dense monolayer and dilutes the PIM along the surface. The choice of solvent for the "inks" is important, as it is necessary that the solvent and solutes do not chemically react with the print head.

Printing Procedure. Inkjet printing was used to create patterned monolayers and binary chemical gradients on surfaces. A Canon BJC-series printer was modified slightly by removing the casing and a few feeding rolls to accommodate feeding of the gold substrates. Also, the print drivers were slightly modified as described by Pardo et al.[13] to account for the differences in the solution viscosities of traditional inks and thiol solutions. The printer resolution for the Canon BJC-series printer used was 720 (vertical) x 360 (horizontal) dots-per-inch (DPI) maximum. The inkjet print head was removed and thoroughly cleaned with deionized water and ethanol to ensure that the ink was completely removed. The cartridges could then be filled with the deposition solutions instead of ink. This cartridge rinsing was also done before each print session. Microsoft PowerPoint was used to design the gradients and patterns, and pattern guides were printed on transparencies with black ink.

The cleaned gold surfaces were then secured to the pattern guides using double-sided Scotch tape. The previously cleaned ink tanks were then filled with the monolayer solution(s), and patterns were then printed. The ethanolic solutions dried almost immediately upon printing on the surfaces, but to ensure dryness, the surfaces were dried after printing with a gentle stream of nitrogen. A slight spreading of the printed solutions on the substrate before drying was observed; however, as will be shown, the shape of the pattern was preserved even with this slight spreading of ink on the substrate. With such small droplets being printed, it seems reasonable to suggest that the rate of solvent (ethanol) evaporation dominates over the spreading rate, and hence the printed pattern is preserved. After drying, the samples were rinsed with ethanol and then dried again.

The designs printed can be color-coded with each color representing a particular deposition solution. The Canon BJC printer cartridge has four different ink tanks, corresponding to cyan, magenta, yellow, and black. By using these four colors in PowerPoint, we are able to access each ink tank (monomer solution) independently. Thus, up to four "inks" can be printed simultaneously in a given design; however, in these studies, only binary systems were studied, which allowed us to print one component and then backfill with the second, if desired. These patterns and gradient monolayers containing the PIM serve as a platform for subsequent ATRP to make patterned and gradient thin polymer films.

ATRP Chemistry. ATRP was used for polymerization of methyl methacrylate from the PIMs that are printed onto the surface. In a sense, ATRP is simply the tool used to amplify the printed patterns in the direction normal to the surface. ATRP was carried out at room temperature using an organometallic catalyst complex comprised of Cu(I)Cl and the ligand hexamethyltris(2-aminoethyl)amine (Me_6TREN) in a 1:1 molar ratio. Me_6-TREN was synthesized by methylation of tris(2-aminoethyl)-amine.[14] The organometallic catalyst complex of Me_6TREN and Cu(I)Cl was added to a 2 M monomer solution and this mixture was then subjected to several freeze−pump−thaw cycles to remove dissolved oxygen and then transferred to a glovebox. The initiator-coated surfaces were then immersed in the monomer and catalyst solution, and the polymerization was allowed to proceed for a fixed period of time, normally 24 h, to grow thick polymer brushes. The polymer-modified surfaces were washed with toluene and dried with a stream of nitrogen prior to characterization.

Results and Discussion

Gradient Monolayer Surfaces. To make gradient monolayers, dodecanethiol was printed in a gradient pattern onto the surface and the sample was then backfilled with MUT to form a binary chemical gradient. It was determined that backfilling, as opposed to printing the second thiol, led to a better quality monolayer; however, the backfilling of the printed monolayer with the second thiol had to be done very quickly (1−2 s dip

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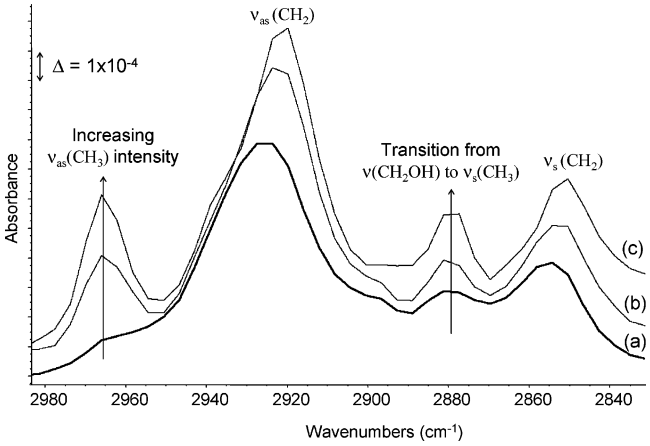

Figure 2. FTIR-ER spectra from three different positions along a printed gradient monolayer of dodecanethiol backfilled with 11-mercaptoundecanol with zoom into the region where CH_2 and CH_3 stretching modes appear. (a) Edge of sample rich in $-$OH-terminated groups; (b) center of sample; (c) edge of sample rich in $-CH_3$-terminated groups.

time in backfilling solution). If the backfilling was done for longer than a few seconds, the backfilling thiol would replace the printed thiol monolayer on the surface. This is due to the fact it takes much longer to form a stable thiol-based monolayer than the few moments between when a printed droplet impacts the surface and the solvent evaporates. A representative FTIR-ER spectrum of a sample made by this protocol is shown in Figure 2. Results were consistent, provided the completely defined protocol was followed.

As seen in Figure 2, the spectrum for the end of the sample that is rich in the hydroxyl ($-$OH)-capped MUT shows peaks at 2850, 2879, and 2919 cm^{-1}, while the end of the sample that is rich in the methyl ($-CH_3$)-terminated monolayer species has an additional peak at 2962 cm^{-1}. The peaks at 2850 and 2919 cm^{-1} are due to symmetric and asymmetric stretching of the methylene ($-CH_2$) groups, respectively. The mode at 2879 cm^{-1} is due to the stretching of the C$-$O group of the hydroxyl-terminated monolayer species. The methyl-capped monolayers have peaks at 2850 and 2919 cm^{-1}, also due to methylene stretching modes, as well as peaks at 2962 and 2877 cm^{-1} that are due to the symmetric and asymmetric stretching modes of the terminal CH_3 group, respectively. These spectra confirm that the printed and backfilled monolayers display the expected binary chemical gradient, and the positions of the methylene stretching modes indicate that the monolayers are ordered.[15]

Static water contact angle results more fully demonstrate the gradual transition from hydrophilicity to hydrophobicity along the gradient: The measured water contact angle at the MUT-rich edge was 38° ± 2°, while the measured water contact angle at the 1-dodecanethiol-rich edge was found to be 84° ± 2° (Figure 3). Although a transition is evident from these results, the contact angles on both the edges differ from the expected values (20° for self-assembled monolayers (SAMs) made from MUT and 110° for SAMs made from 1-dodecanethiol).[16] We suspect that these differences in contact angle are due to rearrangement that occurs during backfilling and/or are caused by the fact that the inkjet printer ejects discrete drops of monolayer-forming solution onto the substrate. Hence, the inherent feature resolution of the printer limits the mesoscopic coverage of the printed material on the surface. Nevertheless, clear evidence of the gradient is observed in Figure 3, which shows the change in the shape of the water drops placed on a gradient surface. The water contact angle decreases as we move from the right side (dodecanethiol rich) to the left side (dodecanethiol lean) of the substrate.

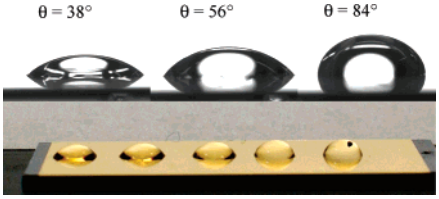

Figure 3. Images of static water droplets along a binary gradient monolayer made by printing of dodecanethiol followed by backfilling with 11-mercaptoundecanol.

The incapacity of the printer to print monolayers that uniformly cover the entire surface can be explained by understanding the feature resolution. The images printed by an inkjet printer are comprised of pixels. Each pixel is comprised of many ink dots. Binary gradients are printed on the surface by varying the number (surface density) of ink dots within a given pixel. As we move from one edge of the gradient to the other, the ink dot density within the pixels changes. For example, when a gradient is made by printing only a single color "ink", the dot density within the pixels decreases along the gradient and the other spots are left vacant. The systematic variations in the relative amounts of these "vacant" and printed dots within the pixels in the graded direction produce the gradient. Thus, the observed deviation in the contact angle data is due to fact that the printed monolayers are not fully covering the surface: there are vacant spots on the substrate, and during backfilling after printing, these vacant spots become occupied by the second component. This is also consistent with our finding that better quality binary monolayers were produced by backfilling, rather than printing the second component.

Polymerized Gradient Surfaces. For growing PMMA brushes, the dithiol-based ATRP initiator was printed onto a gold substrate.[12] The pattern created by printing the PIM on the surface would be amplified by the polymerization. The assembly of the initiator onto the surface is done by feeding a pattern or gradient to the printer through the attached computer. After the PIM was printed on the surface and the layer backfilled with dodecanethiol, ATRP was used to grow PMMA from the surface using the procedure mentioned earlier. FTIR-ER spectra shown in Figure 4 confirm the presence of the printed PIM and PMMA on the surface.

The polymer gradient was evident visually and was also confirmed using AFM (Figure 5). One could also see the gradient if one exhaled on the sample: The exhaled vapor preferentially condensed on the more hydrophilic side of the substrate, whereas no condensation occurred on the hydrophobic side. The polymer-rich edge was found to have higher roughness (RMS roughness = 30 nm) than the edge that was not printed with the bromo-initiator (RMS roughness = 5 nm). After polymerization, an average height differential of 100 nm was observed between the highest and the lowest features on the edge of the substrate that had high initiator density. As we move along the gradient, a decrease in height differential is measured: the edge with lower initiator density shows an average height differential of 15 nm. AFM images also indicated that polymer growth occurred in distinct regions and was

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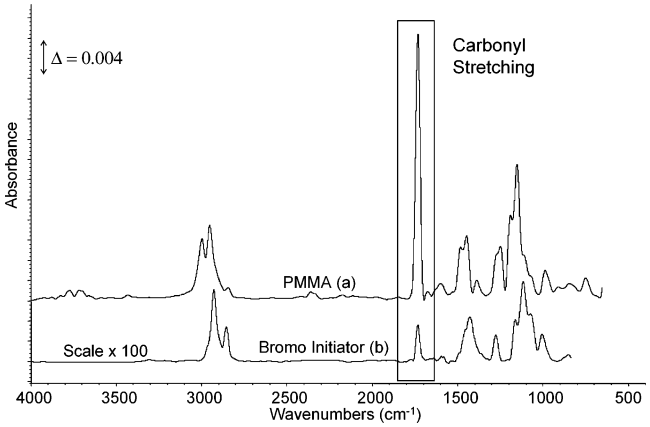

Figure 4. FTIR-ER spectrum showing the characteristic stretching peaks for (a) PMMA and (b) bromo-initiator used for ATRP. As indicated, the scales used in the two spectra are not the same.

not homogeneous. We believe that this occurs because, as with printing of the CH_3-capped monolayers, the printing of the initiator onto the surface is a result of discrete drops of the initiator solution from the ink cartridge nozzle impinging onto the surface. These distinct regions appear as polymer spots/features that are, on average, 15 μm apart from each other, which could be defined as the feature resolution of the process after polymerization (Figure 5b).

Polymerized Patterned Surfaces. To test the fidelity of printing, various initiator patters were printed and analyzed. A higher-resolution printer would give finer features and smaller pixels, and consequently a higher pattern resolution, compared to the low-end printer used here. The pattern fidelity would be expected to be even lower for complex designs with this low-end printer since a complex pattern requires greater drop-placement accuracy in order to achieve critical pixel sizes. In undertaking these tests, we found that we were limited in our ability to amplify fine patterns because of the pattern resolution of the printer. Also, our ability to "find" patterns a few hundred micrometers in width on a macroscopic surface with a nanoscopic technique like AFM (maximum image width of 115 μm), would be constrained. Hence, we printed patterns with millimeter-sized features and used optical microscopy to find and examine the patterns.

Figure 6 shows digital pictures of two patterned substrates—a cross and a hole—that were distinct and could be observed visually. The cross shown in Figure 6a was formed on the surface by printing the bromo-initiator as the cross and backfilling with the CH_3-capped spacer. The left edge of this cross was damaged by tweezers during handling. Polymerization occurred at the initiator sites, whereas no polymer growth is seen in the region around the cross where the spacer was assembled. The reverse pattern was also tested where the spacer was printed as the cross and the sample then backfilled with the bromo-initiator (Figure 6b). The hole pattern had the spacer printed at the center of the substrate and the sample was backfilled with bromo-initiator to achieve polymer growth everywhere except where the spacer was printed (Figure 6c). Although the images seen in Figure 6 appear grainy, it is an artifact that occurs during flash photography due to the reflective nature of the gold substrate.

An optical microscope (Olympus BX-60) was used to view the patterns more closely. As seen in Figure 7, the patterns showed distinct boundaries. The common problem encountered during inkjet printing is confining the spreading of the sprayed solution drops on the surface since spreading limits the pattern resolution. The pattern resolution controls the ability of the printer to print a pattern or a graphic with distinguishable boundaries. Hence, a pattern resolution of 360 DPI signifies that the transition between two adjacently placed pixels occurs within 70 μm. This should not be confused with the feature resolution, as multiple features make a single pixel and several pixels form a pattern. The optical micrographs seen in Figure 7 illustrate that the transition from the polymerized region to the nonpolymerized region occurs within approximately twice the pattern resolution. This means that a little spreading of the DOD-printed monolayers occurs when these patterns are printed onto surfaces. While this spreading tends to distort the pattern

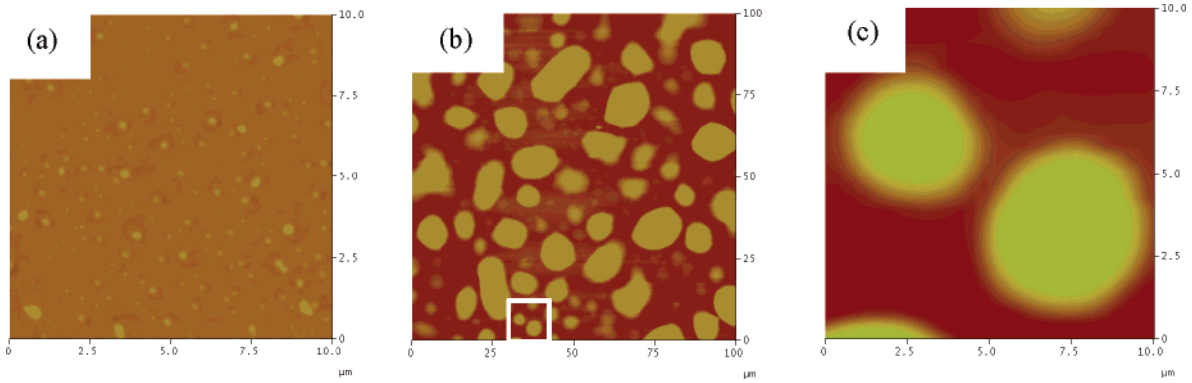

Figure 5. AFM height images taken along the gradient. (a) 10 μm × 10 μm region from the polymer-lean edge; (b) 100 μm × 100 μm region from the polymer-rich edge; (c) 10 μm × 10 μm region from polymer-rich edge taken from the boxed area shown in (b).

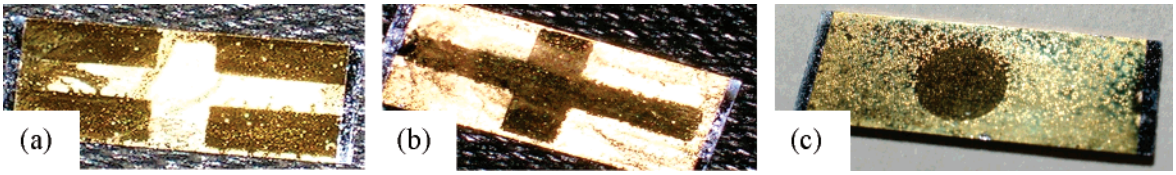

Figure 6. Digital pictures of cross and hole patterns after polymerization with PMMA on gold substrates. The dark regions correspond to no polymer growth, while the light regions are where the polymer was grown. The graininess of the images is an artifact that occurs during flash photography due to the reflective nature of the surfaces.

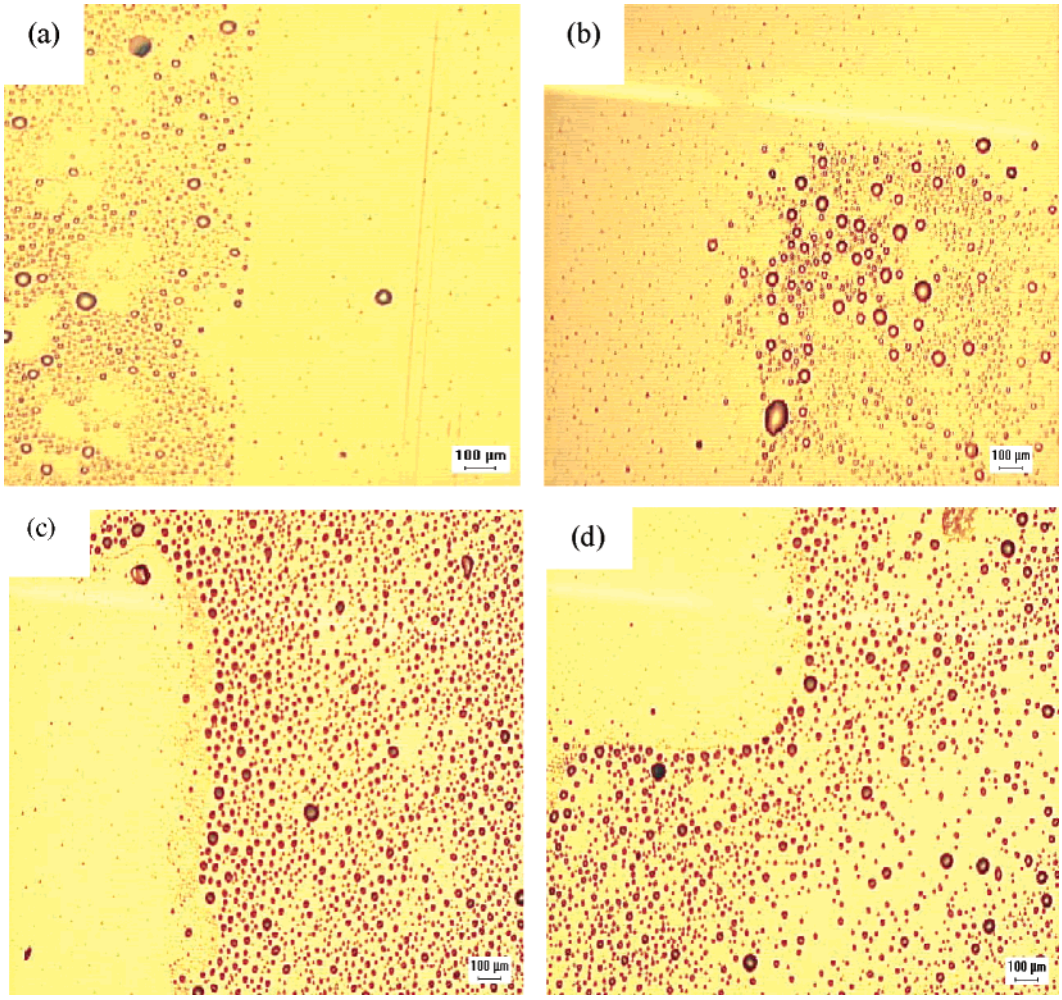

Figure 7. Optical images of the cross patterns showing the boundary between the polymer and spacer interface: (a) and (b) images showing the boundary between the methyl-terminated spacer printed as a cross with no polymer growth occurring in this region surrounded by the polymerized region (corresponds to Figure 6b); (c) and (d) images showing the boundary between the initiator printed region amplified as the polymerized cross surrounded by the spacer region (corresponds to Figure 6a).

boundaries, in view of the pattern resolution, the pattern fidelity seen in Figure 7 agrees with expectations.

Conclusions

We have demonstrated that DOD-based inkjet printing can be used to form patterned and gradient monolayers on substrates. FTIR-ER and contact angle measurements verified that gradient monolayers were formed. The contact angle measurements showed a continuous change in contact angle along the graded surface. Controlled deposition and patterning of printed monolayers along the surface coupled with ATRP can be used to amplify the printed pattern and create tailored soft surfaces. Well-defined patterns can be obtained by precise placement of ATRP initiator molecules onto the substrate, and the definition and fidelity of the polymerized layers agree with what is expected on the basis of pattern resolution. It is anticipated that this technology can easily be transferred to a variety of substrates, including flexible polymer films. The advantage of having automated control with simple computer software and high throughput makes inkjet printing coupled with ATRP a viable choice for making micropatterned, polymer-modified surfaces with high throughput.

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