Microstructures of poly (ethylene glycol) by molding and dewetting

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We report on the fabrication of microstructures of poly (ethylene glycol) (PEG) using a soft molding technique. When a patterned poly (dimethylsiloxane) stamp is placed on a wet PEG film, the polymer in contact with the stamp spontaneously moves into the void space as a result of capillary action. Three types of microstructures are observed with the substrate surface completely exposed: a negative replica of the stamp, a two-dimensional projection of the simple cubic structure, and a two-dimensional projection of the diamond structure. A molding process is responsible for the first type and a dewetting process for the final two. A phase diagram is constructed based on the effects of molecular weight and concentration, which shows that mobility and confinement play a crucial role in determining the particular type of microstructure obtained. The PEG microstructure could be used as a lithographic resist in fabricating electronic devices and a resistant layer for preventing nonspecific adsorption of proteins or cells. © 2003 American Institute of Physics.

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Molding of polymer melts is the traditional manufacturing technology of plastics and, in general, has been developed in the form of injection molding, in which a raw plastic material is melted and then injected into a mold through a nozzle by applying pressure. In the early 1990s, a soft, elastomeric stamp like poly (dimethylsiloxane) (PDMS) was introduced as a new element for molding of polymers, precursors and sol gels. Since then, a number of unconventional, useful molding techniques have been developed such as micromolding in capillaries, solvent-assisted microcontact molding, microtransfer molding (μTM), replica molding, capillary force lithography, and soft molding (SM). Of these, SM provides a convenient way to fabricate polymeric microstructures when the polymer is liquid or wet after spin coating. The technique generally consists of three steps: placing a patterned PDMS stamp on the surface of a spin-coated polymer film, allowing the stamp to absorb solvent, and then letting the stamp and the substrate remain undisturbed for a period of time.

Poly (ethylene glycol) (PEG) is a nondegradable, hydrophilic polymer that can be cross-linked into hydrogels using photopolymerization reactions by acrylate functional groups. Although much work has been done with regard to patterning of PEG hydrogels using photolithography, there essentially has been no soft lithographic technique to pattern PEG hydrogels directly on the surface. Contact angle measurements show that PEG dimethacrylate is slightly hydrophobic (~65°), which does not affect the overall results, however.

PDMS stamps were fabricated by casting PDMS (Sylgard 184 Silicon elastomer, Essex Chemical) against a complementary relief structure prepared by a photolithographic method. To cure, a 1:10 ratio of the curing agent and the pre-polymer were mixed and incubated at 70 °C for 1 h. PDMS was then detached from the master and cut. The stamp had protruding (positive) boxes with four different lateral dimensions: 3, 5, 7, and 10 μm with a constant step height of 1.5 μm. Silicon dioxide and glass were used as the substrates. Prior to spin coating, the substrates were cleaned by rinsing with acetone and ethanol several times to remove excess organic molecules and dried in a nitrogen gas stream. To investigate the effects of molecular weight (MW), four different molecular weights were tested: 330, 550, 1000, and 4600. For MW of 330 and 550, PEG dimethacrylates were used for cross-linking. Various concentrations of PEG or PEG dimethacrylate solution in methanol (1, 2, 5, 10, 20, 50, 70, and 100 wt % or pure PEG dimethacrylate) were prepared. For liquid PEGs, 1 wt % of the UV initiator (2,2-dimethoxy-2-phenylacetophenone) with respect to the
amount of polymer was added in the solutions. The polymer was then spin coated (Model CB 15, Headaway Research, Inc.) onto a substrate at 3000 rpm for 10 s. The film thickness ranged from 60 nm to 1.2 μm as measured by ellipsometry. The patterned PDMS stamp was carefully placed onto the surface to make conformal contact and the stamp and the substrate remained undisturbed for a period of time, typically, for 30 min. For liquid PEGs, the samples were placed for 2 h under a 365 nm, 15 mW/cm² low-power black-light inspection lamp (ELC-251, Electro-Lite Corp.) for cross-linking.

Figure 1 outlines the procedure and three types of microstructures that are observed in our experiment along with the typical optical images. The structures result from two processes: molding and dewetting. The schematic diagram on the left hand side depicts the molding process, in which a negative replica of the stamp forms on the surface (type I). On the other hand, the two diagrams in the middle and the right hand side illustrate the dewetting process. Such dewetting patterns can be classified into two types. The first pattern resembles the two-dimensional projection of simple cubic structure (type II) and the second the two-dimensional projection of diamond structure (type III). A notable finding in dewetting patterns is that there are no traces of the original PDMS stamp, which indicates that capillary rise is completely suppressed. In comparison to this, capillary rise cannot be suppressed in the case of a hydrophobic polymer (i.e., polystyrene) such that traces of the stamp are always observed on the surface after dewetting. These dewetting patterns would be useful for templating two-dimensional photonic crystals and stacking into three-dimensional assembly.

The three types of microstructures turn out to be highly dependent on the molecular weight and concentration of PEG, which is clearly shown in a phase diagram in Fig. 2. A 10 μm box pattern was used for this phase diagram. As seen from the figure, the molding process dominates throughout all the molecular weights as long as the concentration is relatively high. This can be readily understood in that the film thickness would be high enough to fill up the void space of the stamp as the concentration increases. Once the void space is fully taken up, no dewetting can be observed, which may be referred to as the “confinement” effect. On the other hand, the demarcation line between the molding (type I) and the dewetting (type II and type III) is also dependent on the molecular weight such that the tendency toward the molding increases as the molecular weight increases. This result can be attributed to the effects of mobility of PEG, which can be termed as the “mobility” effect. If the molecular weight is relatively low (<1000), the polymer has a large mobility, thereby easily achieving the thermodynamically equilibrium condition (i.e., the dewetting structure in this case). By contrast, the movement of polymer chains will be strongly restricted under the confinement of the stamp if the molecular weight is relatively high. This argument can be further supported by another boundary line between type II and type III structures in the bottom region in Fig. 2. The fact that the type III structure dominates for high molecular weight reveals that small polymer islands are frozen during the molding process due to the confinement and they are observed after the stamp removal. In the phase diagram, there is a transition region, in which the molded and dewetted structures can coexist. The transition window appears to get smaller as the molecular weight increases. If the pattern size goes smaller, i.e., less than 10 μm, a type I structure can be seen at lower concentrations (the demarcation line moves downward) and a type II structure at higher molecular weights (the demarcation line moves right).

The molded and dewetted PEG microstructures provide a number of potentially useful technological applications since the substrate surface is completely exposed for all the three types of structures. With regard to optical lithography or photolithography, this is of major interest because a residual layer is a problem for most molding techniques. If the surface can be exposed, there is essentially no difference between the molding and photolithography in that the molding step completely replaces the exposure and developing steps in photolithography. In addition, the patterned PEG sur-
the surface was imaged using an inverted microscope and water several times and drying in a stream of nitrogen, in the solution for 30 min. After rinsing with PBS solution to reduce protein adsorption, we prepared fluorescing simple electronic devices. could replace the current photolithographic process in fabrication sizes. If the edge profile and etching conditions are tailored to meet the stringent pattern fidelity, the molding step would provide sharp contrast in the fluorescent image. The scale bar indicates 10 μm.

To examine the effectiveness of the PEG pattern and surfaces to reduce protein adsorption, we prepared fluorescein isothiocyanate-labeled bovine serum albumin (FITC-BSA). FITC-BSA was dissolved in 10 mM phosphate buffered saline (PBS) solution (pH = 7.4). The PEG pattern was prepared on glass substrate and the samples were immersed in the solution for 30 min. After rinsing with PBS solution and water several times and drying in a stream of nitrogen, the surface was imaged using an inverted microscope (Axiovert 200, Zeiss). Figures 3(c) and 3(d) show 5 μm lines of PEG pattern on glass substrate (c) and the corresponding fluorescent image (d). As expected, most BSAs deposited on the exposed glass surface, which shows a spatially well-defined protein pattern. This indicates that the cured PEG film also provides protein resistance as with PEG terminated self-assembled monolayers. Although not shown, the protein pattern could be reduced below 1 μm with suitably prepared PDMS stamps over large areas.

In summary, we have fabricated PEG microstructures using the soft molding technique and tested their effectiveness as a resist for pattern transfer and a resistant layer for the adhesion of proteins. Three types of microstructures are observed depending on the competition between molding and dewetting process. To elucidate the competition, a phase diagram is constructed based on the effects of molecular weight and concentration, which reveals that confinement and mobility can account for the complex behavior of PEG polymer within the PDMS stamp. The PEG microstructures presented here could provide a new way of fabricating simple electronic and biological devices and studying dewetting behavior in a repulsive environment.

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