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Versatile Stamps in Microcontact Printing: Transferring Inks by Molecular Recognition and from Ink Reservoirs

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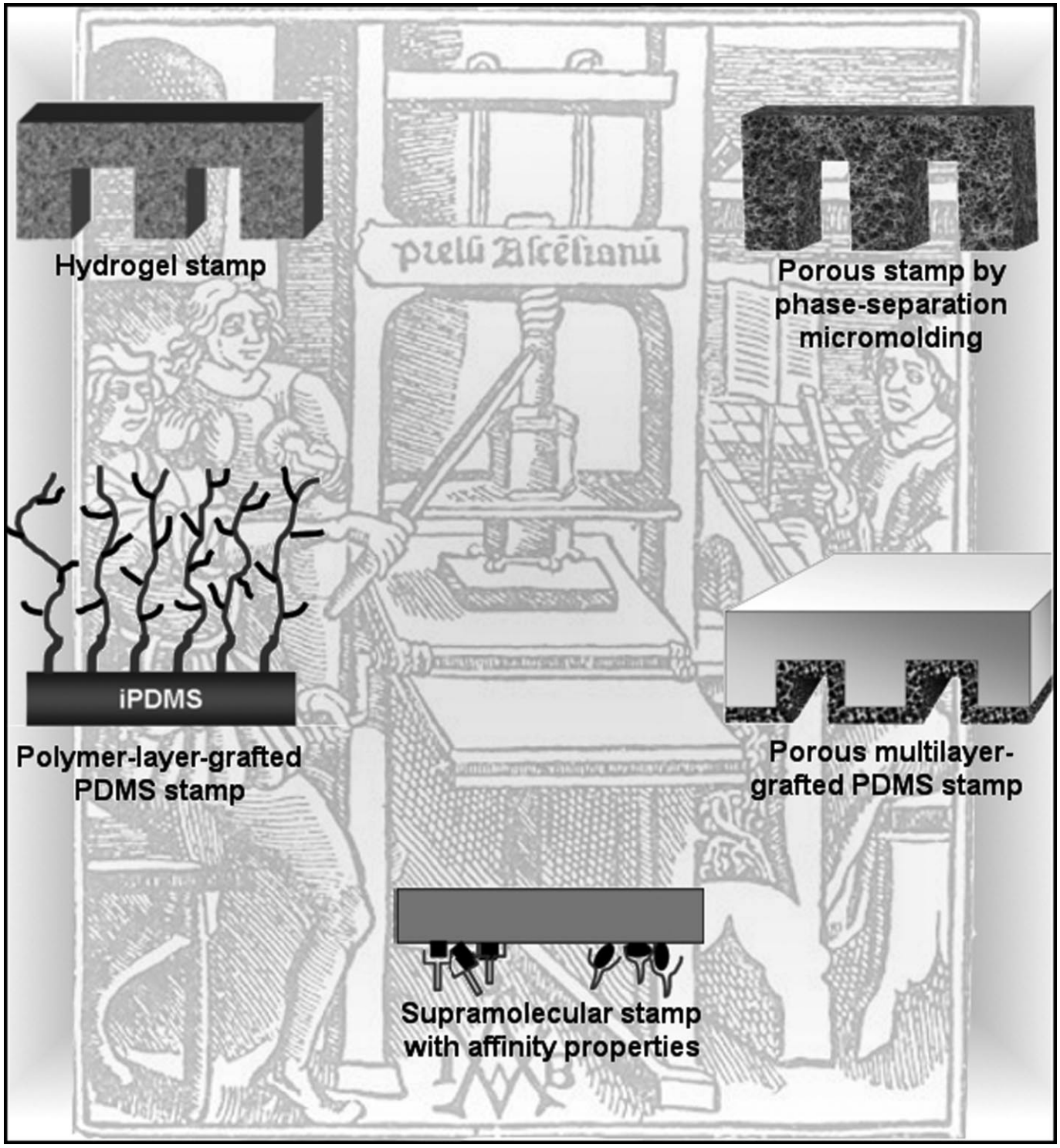

Abstract: Microcontact printing is a heavily used surface modification method in materials and life science applications. This concept article focuses on the development of versatile stamps for microcontact printing that can be used to bind and release inks through molecular recognition or through an ink reservoir, the latter being used for the transfer of heavy inks, such as biomolecules and particles. Conceptually, such stamp properties can be introduced at the stamp surface or by changing the bulk stamp material; both lines of research will be reviewed here. Examples include supramolecular stamps with affinity properties, polymer-layer-grafted PDMS stamps, and porous multilayer-grafted PDMS stamps for the first case, and hydrogel stamps and porous stamps made by phase-separation micromolding for the second. Potential directions for future advancement of this field are also discussed.

Keywords: host–guest systems · layer-by-layer assembly · microcontact printing · microporous materials · phase-separation micromolding · supramolecular interactions

Introduction

Among the existing soft lithographic patterning techniques, microcontact printing (μCP), which employs a micropatterned stamp to transfer molecules as an ink to a surface, has proven to be a very versatile surface modification method in materials and life science applications.[1] For μCP, the elastomer poly(dimethylsiloxane) (PDMS) has been most widely used as a stamp material to generate surface patterns and structures ranging from about 100 nm to many μm, owing to properties such as conformal contact with solid substrates, optical transparency, and chemical inertness. In the past few years, a lot of work has been done to improve the low mechanical stability of PDMS and to solve the ink diffusion problem.[2–9] Besides mechanical properties, surface modification of PDMS to tune its wetting behavior in the printing of a variety of functional materials is also widely studied.[10–12]

Unlike the printing of small apolar ink molecules, such as alkanethiols, that can be absorbed inside the stamp and then transferred upon contact between the stamp and substrate, the printing of heavy inks, such as nanoparticles and proteins, is much more difficult due to their larger size and concomitant lower diffusivity. Heavy inks can not be absorbed by a regular PDMS stamp but merely adhere to the stamp's outer surface. Therefore, reinking is necessary after every step.[1] Some stamp materials that can potentially provide a reservoir for such inks and thus permit the continuous multiple printing of heavy inks are, therefore, being developed. This concept article mainly focuses on the fabrication of universal stamps for binding and releasing inks, mostly heavy inks. These stamps include: 1) surface-functionalized stamps and 2) bulk stamp materials with reservoir properties.

Surface-Functionalized Stamps

The least invasive option to tailor the ink-recognition properties of a stamp for microcontact printing is to tune its surface while maintaining the bulk (typically PDMS) as a support to preserve benevolent properties, such as conformal contact. The surface of PDMS can be readily changed, typically by employing a mild oxidation step followed by a chemical functionalization by using silanes. The surface-functionalized stamps covered here include: 1) supramolecular stamps with affinity properties, 2) polymer-layer-grafted PDMS stamps, and 3) porous multilayer-coated PDMS stamps.

Supramolecular stamps with affinity properties: Supramolecular interactions (hydrogen bonding, π–π interactions, hydrophobic interactions, etc.) play an important role in biology and are being extensively used for other nonbiological applications as well.[13] The reversible nature of the supramolecular interaction between complementary host–guest pairs offers flexibility, controllable binding strength, and dynamics for the controlled positioning of molecules, assemblies, and particles on a substrate.[14] The integration of supramolecular host–guest interactions into μCP leads to improvements in the nanopatterning of (bio)molecules, as discussed below.

Affinity microcontact printing (αCP) was first developed by Bernard and co-workers around eight years ago.[15,16] This method uses a structured PDMS stamp functionalized with ligands that recognize target molecules. After the target molecules have been captured at the ligand-covered stamp surface, they are transferred from the stamp onto the desired substrate. The ligands remain on the stamp for reuse. Bernard and co-workers functionalized the surface of PDMS with anti-mouse IgG, which selectively captured labeled mouse IgG from a crude biological sample.[15,16] After

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rinsing off nonspecifically bound molecules, the stamp was brought into contact with the substrate. Because of the stronger substrate–protein interaction compared with the stamp–protein interaction, the captured molecules were transferred to the solid surface, as shown in Figure 1. αCP has the potential to be a versatile tool for extracting, affinity purifying, concentrating, and patterning precious biomolecules in a single step.[17]

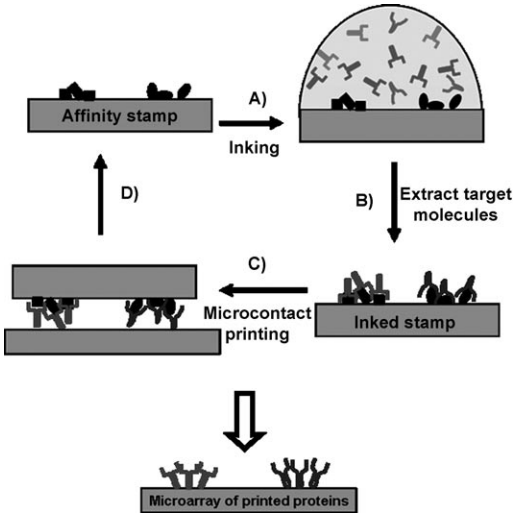

Figure 1. Microarrays of proteins on surfaces can be fabricated by using an affinity stamp derivatized with various capture sites that can extract target biomolecules from a complex mixture and transfer them onto a surface in a single microcontact printing step. Arbitrary protein patterns on the affinity stamp are prepared on an activated stamp by using microwells.[15,16]

Similarly, single-strand DNA was immobilized on a stamp and subsequently interacted with chemically functionalized complementary DNA to achieve specific inking. Crooks et al. reported a method for transferring biotin-functionalized hybridized DNA from PDMS stamps to streptavidin-modified surfaces based on the affinity between biotin and streptavidin.[18,19] Simultaneously, Stellacci developed a similar method called supramolecular nanostamping (SuNS) that transfers single-strand DNA with high resolution.[20,21]

Recently, we demonstrated the preparation of β-cyclodextrin (β-CD) receptor-functionalized PDMS stamps and reported the selective recognition of ink molecules based on specific and directional supramolecular host–guest interactions.[22] The receptor-covered stamps exhibited a very high selectivity for ink molecules with complementary guest moieties as compared with inks that lacked them; this was also true of mixtures of such inks. Uniform, equilibrium-controlled ink transfer was achieved upon conformal contact between the β-CD-covered stamp and the substrate (Figure 2). By using an ink monolayer assembled on a β-CD surface as a supramolecular inkpad, control over the amount of transferred ink molecules was shown. This work may aid the selective attachment of molecules to functional

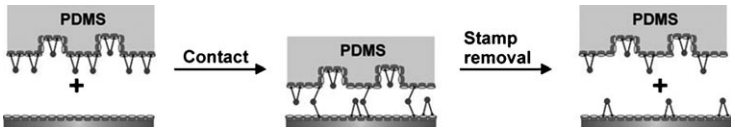

Figure 2. Supramolecular microcontact printing of guest-functionalized ink molecules from a β-CD receptor-functionalized PDMS stamp onto a receptor-covered substrate.[22]

surfaces with high specificity, which is crucial for the development of (bio)sensors.

Polymer-layer-grafted PDMS stamps: A polymer layer grown on a PDMS stamp surface can potentially be used as an ink reservoir, thereby enabling controlled ink binding and site-selective ink delivery. A number of strategies have been developed for the attachment of a polymer layer to a PDMS surface. These can be divided into two categories: physisorption and chemical coupling.

Physisorption of polymers to a PDMS surface can be steered by electrostatic forces. Recently, so-called dendristamps were fabricated by Reinhoudt et al. by the adsorption of positively charged, fifth generation poly(propylene imine) dendrimers (G5-PPI) to a negatively charged, oxidized PDMS surface.[23] The adsorption process results in a high density of positive charge on the stamp surface that can attract negatively charged DNA and RNA molecules. As shown in Figure 3, PDMS stamps modified in this way were used to transfer DNA to suitable solid supports to create patterns characterized by a more homogeneous distribution and higher coverage than those created by using normal 3-aminopropyltriethoxysilane (APTES)-modified PDMS. However, because G5-PPI is not covalently attached to the stamp it sticks to the DNA and is (partially) transferred to the target substrate upon printing.

Chemical coupling onto PDMS leads to a higher stability compared with physisorption, but is more difficult to achieve because PDMS is chemically inert. Typically, PDMS stamps have to be first treated with reactive oxygen species (O_2 plasma or UV/ozone) followed by chemical grafting of polymers with reactive end groups to the oxidized PDMS stamps. The presence of a thick (compared with the size of an ink molecule) hydrophilic layer on the surface of a stamp (Figure 4) is beneficial for transferring large amounts of polar substances to a surface.[24–26]

Recently, polyelectrolyte brushes, which act as ink reservoirs, were successfully grown on PDMS stamps by Huck et al.; they enable the controlled uptake and site-selective delivery of ionic species.[27] Huck et al. used surface-initiated cationic poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMETAC) brushes. These brushes were grown from initiator-modified PDMS stamps by using aqueous atom-transfer radical polymerization (ATRP).[28] The inks were preconcentrated on the stamp surface within the ion-exchanging/ion-pairing sorbent PMETAC brush layers. Therefore, selective delivery and loading of the inks be-

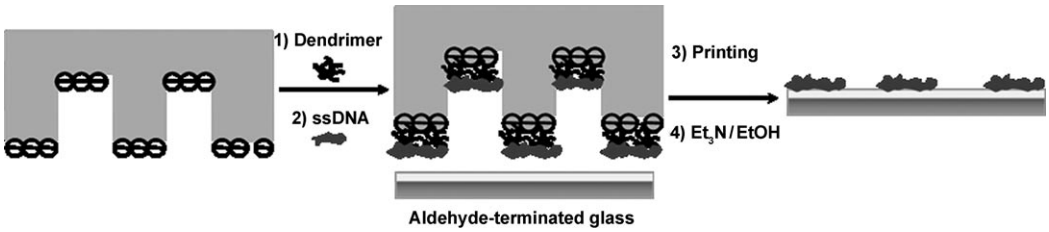

Figure 3. Microcontact printing of DNA with dendri-stamps. An oxidized PDMS stamp is first inked with dendrimers and subsequently incubated with fluorescein-labeled DNA. After transfer printing the DNA onto the solid support, the substrate is rinsed with EtOH/Et_3N to wash cotransferred dendrimers from the substrate.[23]

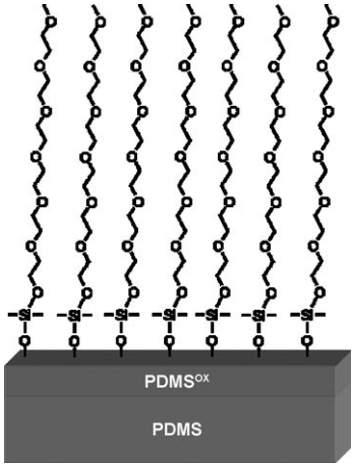

Figure 4. Hydrophilic poly(ethylene glycol) chains attached to oxidized PDMS.

comes possible and resembles the printing of hydrogel stamps (see below).

A similar method was developed by Ma et al.[29] As shown in Figure 5, initiator-integrated PDMS (iPDMS) was simply prepared by mixing a vinyl-terminated initiator, Sylgard 184 PDMS prepolymer, and a curing agent. After curing, the initiators were present at the surface, which allowed further surface modification. Subsequent ATRP from iPDMS endows the PDMS tunable surface properties. For example, surface-initiated polymerization was used to render the PDMS surface superhydrophobic.[30] This combination of iPDMS and ATRP thus allows the tailored surface modification of PDMS.

At almost the same time, Huck et al. developed a way to selectively modify the surface of PDMS through minimization of interfacial free energy by the self-assembly of functional molecules at the surface, which mirrored the distribution of surface energies on a template (Figure 6).[31] The chemically patterned flat PDMS surfaces can then be further amplified by surface-initiated polymerization. This method allows a straightforward modification of PDMS with a wide range of functional groups into patterns with controlled dimensions. It is applicable not only to planar structures, but also to nonplanar surfaces. Because no oxygen plasma treatment is used in this process, no cracks are generated on the PDMS surface, which gives the poten-

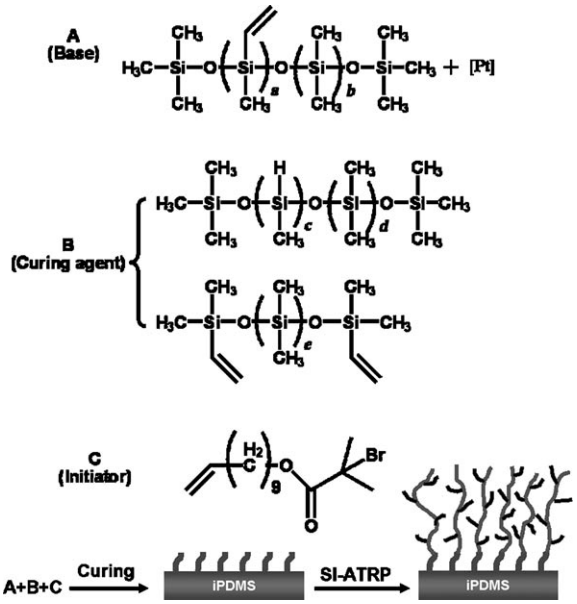

Figure 5. Preparation of iPDMS and permanent surface modification of iPDMS by SI-ATRP.[29]

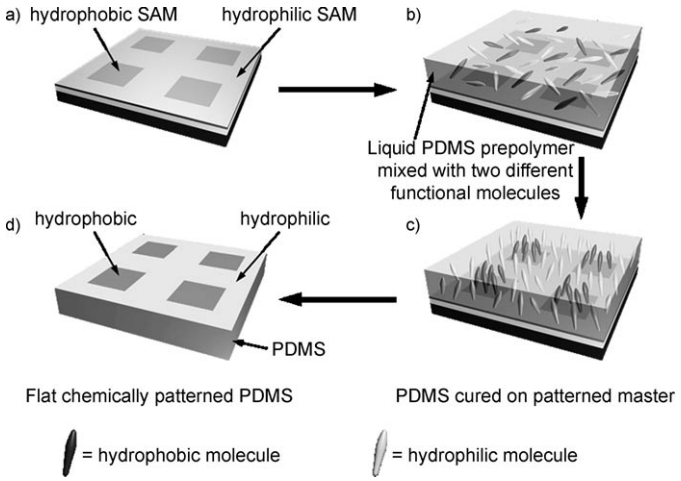

Figure 6. a) A microcontact printed and backfilled SAM substrate on Au with a large surface energy contrast between the two components is used as a chemical template; b) PDMS prepolymer is mixed with two different functional molecules (a polar and a less polar alkene) and poured over the master; c) the alkenes self-assemble on the functionalized monolayer and react with the PDMS backbone by hydrosilylation during the curing period; d) upon lift-off, a flat PDMS stamp with two different chemical functionalities at the surface is obtained.[31]

tial to fabricate sub-micrometer features of different chemical functionalities.

Porous multilayer-grafted PDMS stamps: Layer-by-layer (LbL) assembly is a powerful method of fabricating ultrathin films.[32] The popularity of this method arises from its simplicity, versatility, and systematic control over the structure and the thickness of the resulting film. Exposure of a LbL multilayer to solutions with different pH values or ionic strengths can lead to the formation of micro- or nanoporous structures.[33]

Very recently, we demonstrated the fabrication of porous LbL-PDMS stamps by multilayer formation on top of PDMS by hydrogen bonding, followed by base treatment and subsequent crosslinking (Figure 7).[34] The pore structures act as an ink reservoir for the absorption of protein inks, which allows multiple printing of the Fc fragment of a human immunoglobulin without the need for reinking; this could not be achieved by printing with normal amino-functionalized PDMS. The main achievement is that stamps were created by which proteins can be transferred from the inside of the stamp, reminiscent of the versatile alkanethiol printing by regular PDMS, surpassing the usually observed mechanism of surface transfer of large molecules, such as proteins by regular and oxidized PDMS. Because the inking is done in aqueous solution and the porous stamps remain hydrated, the proteins are likely to remain bioactive, similarly to the use of hydrogel stamps (see below). With the $\approx$30 nm thick porous multilayer structure used here, multiple prints of protein layers a few nm thick were produced, which indicated significant porosity and use of the porosity for reversible loading of proteins. Because the pore diameter and thickness of the porous films can be tuned by varying the polymer concentration, the number of bilayers, the pH value of the base solution, and the base immersion time,[33] the size of the reservoir of the porous stamp and, therefore, the number of prints that can be performed without reinking can be controlled. Moreover, by using polyelectrolytes with recognition properties, selective ink recognition and transfer can be anticipated with such stamps, as shown above for αCP. Because of the high flexibility of the LbL process, the contact layer of the stamp may be equipped with a polyelectrolyte that suppresses the now observed protein aggregation. Moreover, the same LbL and crosslinking procedure has also been implemented successfully in a dip-pen nanolithography procedure that allows submicron patterning of proteins while retaining biological activity, with the pore structures acting as an ink reservoir.[35]

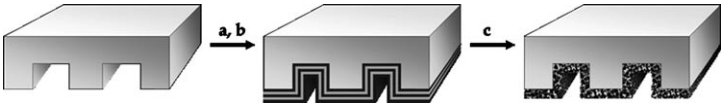

Figure 7. Fabrication of porous LbL-PDMS stamps: a) O_2 plasma and functionalization with *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (TPEDA); b) LbL assembly of poly(4-vinylpyridine)/poly(acrylic acid) (PVPy/PAA) on TPEDA-functionalized PDMS; c) treatment with NaOH and crosslinking.[34]

Bulk-Stamp Materials with Reservoir Properties

Although PDMS has been widely used in microcontact printing, it often suffers from the difficulty of reproducing submicrometer-scale structures resulting from its intrinsically low mechanical integrity and from the difficulty of transferring polar molecules owing to its inherent hydrophobicity. Therefore, bulk-stamp materials have been developed to optimize the mechanical properties for higher print resolution and wetting properties. Compared with surface-functionalized stamps, bulk-stamp materials may have specific advantages: easy preparation, no further modification needed, and the ability to implement porosity, which provides ink reservoir properties. Here, we will focus on stamp materials that have been designed to have reservoir properties, in particular hydrogel stamps and porous stamps made by phase-separation micromolding.

Hydrogel stamps: A hydrogel is a network of water-insoluble polymer chains, sometimes found as a colloidal gel for which water is the dispersion medium. Hydrogels are highly absorbent materials that can contain over 99% water. Owing to this nature, hydrogels are commonly used as scaffolds in tissue engineering, medical electrodes, and sustained-release delivery systems.[36] Patterned hydrogels have been used as stamps for the controlled binding and release of inks.

Martin et al. have developed the hydrogel copolymer of 6-acryloyl-β-o-methylgalactopyranoside and ethylene glycol dimethacrylate, formulated in a 95:5 ratio, which showed good mechanical properties for aqueous microcontact printing applications.[37,38] These lightly cross-linked and highly hydrophilic polymers swell in aqueous media and can adsorb up to 99% water by weight, with an average pore size of 50 nm. These properties are well suited for the transfer of biomolecules, which may denature in nonaqueous environments and which require stamps with large pore sizes for rapid transfer. In addition, the swollen hydrogel acts as a reservoir of material, thereby eliminating the need to reink the stamp. However, due to mechanical insufficiencies, tearing of the stamp upon contact with the substrate can lead to deposition of hydrogel residues.

Grzybowski et al. have described a reactive wet stamping method (r-WETS) based on reaction-diffusion phenomena that allows for simultaneous micropatterning of a substrate with several colored inorganic chemicals.[39–41] Agarose stamps patterned in bas-relief were used and inked with a mixture of inorganic salts that give colored precipitates upon mixing with the salt in the gel. When the protrudes of the agarose stamps are brought into conformal contact with the surface of dry gelatin films, the salt solutions diffuse, react, and precipitate in the gelatin matrix (see Figure 8). With this technique, micropatterning of surfaces with several

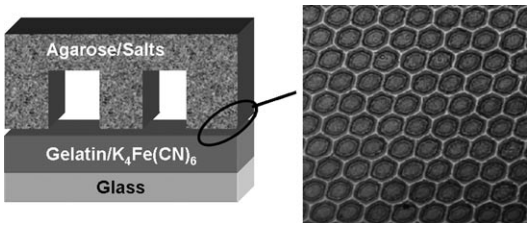

Figure 8. Multicolor patterning of ionically doped gels by salt solution-inked agarose stamps (e.g., $CoCl_2$, $CuCl_2$, or $FeCl_3$). Reproduced with permission from Nature Materials; copyright 2004, Nature Publishing Group.[39]

chemicals at different locations without multiple stamping and registration steps has been realized. The reagents were constantly resupplied from the stamp, and they penetrated into and modified the bulk of the substrate. This technique overcomes the limitation of elastomeric stamps that supply only miniscule quantities of chemicals from the protrudes of the microfeatures, and are thus unsuitable for deep patterning/etching of substrates. It is anticipated that this technique could be used in microscale affinity-based separations and in controlled delivery applications.

Dittmer et al. have explored a rigid self-supporting hydrophilic hydrogel stamp material fabricated by crosslinking the acrylate monomer 2-hydroxyethyl acrylate (HEA) with poly(ethylene glycol diacrylate) (PEGDA) in the presence of water or buffer that can be used to directly print proteins.[42] The high concentration of crosslinker in the prepolymer solution led to a robust hydrogel stamp that had a Young's modulus comparable to that of PDMS while still keeping a good hydrophilicity with a high water/buffer loading capacity for the storage of biological species. This allowed the homogeneous transfer of proteins with micrometer-scale precision. More importantly, the inked proteins remained hydrated and biologically active. However, large biomolecules (150 kDa) are not expected to diffuse into the bulk of the hydrogel stamps but remain adsorbed on the surface.

Porous stamps made by phase-separation micromolding: Phase-separation micromolding (PSμM) is a convenient and versatile microfabrication technique that can be used to structure a broad range of polymers, including block copolymers and biodegradable and conductive polymers, without the need for cleanroom facilities. The method relies on the phase separation of a polymer solution while in contact with a structured mold. Phase separation on a mold mostly results in porosity in a microstructured polymer product that will endow the polymer structure with many fascinating functionalities.[43–45] Hydrophilic porous poly(ether imide)/poly(vinyl pyrollidone) (PEI/PVP) and poly(ether sulfone) (PES)/PVP stamps were successfully fabricated by us by using PSμM (Figure 9). The diameter of the pores was typically around several hundred nanometers, which allowed for encapsulation of large entities, such as nanoparticles of >50 nm. The pore dimensions of the stamps were influ-

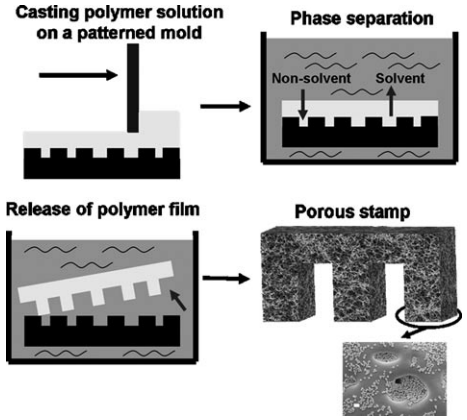

Figure 9. Fabrication of porous stamps by PSμM (bottom right shows SEM images of a porous PES/PVP stamp and one inked with nanoparticles).[46]

enced by varying the polymer blends and the concentration and composition of the blends. By using the porous materials as stamps, heavy polar inks (dendrimers, an Fc fragment of a human immunoglobin, and nanoparticles) were successfully transferred from the stamps to the substrates. With the pore structures functioning as ink reservoirs, multiple printing steps of proteins and nanoparticles were achieved without needing to reink the stamps, which could not be realized by normal PDMS or hydrogel stamps. It is anticipated that this line of research will open new avenues for the direct patterning of large and complex entities (e.g., for microarrays and biodetectors).[46] A limitation of porous PEI/PVP and PES/PVP stamps made by PSμM lies in the comparatively poorer conformal contact compared to PDMS, which makes it difficult to achieve large area patterning. However, with a proper choice of materials used for PSμM, improved elasticity of the porous stamps may be achieved.

Conclusion and Outlook

Versatile stamps for specifically binding and releasing inks can be divided into two categories: stamps with an ink reservoir function (polymer-layer-grafted PDMS, hydrogel stamps, porous stamps made by PSμM, porous multilayer-grafted PDMS), and stamps with a specific affinity (supramolecular stamps). Heavy inks, such as nanoparticles and proteins, can be stored inside a reservoir and transferred to the substrate upon printing. Depending on the method of stamp fabrication, the pore sizes of the reservoir may range from a few nm to hundreds of nm, and may thus be used for size-selective microcontact printing. Combined with molecular surface imprinting (e.g., layer-by-layer surface imprinting[47]), charge selective and chirality selective microcontact printing may also be realized in the near future. However, the mechanical properties of the stamps, such as elasticity and conformal contact, always need to be taken into account during the rational design process. Supramolecular stamps with affinity properties are good candidates for recognizing

and transferring specific inks. The design of supramolecular stamps in a simple way that can facilitate the transfer of multiple inks at the same time is still a great challenge.

Acknowledgements

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