

Effect of Ink Molecular Weights and Annealing Conditions on Molecular Transfer Printing

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Abstract The molecular transfer printing (MTP) technique has been invented to fabricate chemical patterns with high fidelity using homopolymer inks. In this work, we systematically studied the effects of the molecular weights of homopolymer inks and transfer conditions on the MTP process. We explored a large range of molecular weights (~ 3.5 – 56 kg·mol⁻¹) of hydroxyl-terminated polystyrene (PS-OH) and hydroxyl-terminated poly(methyl methacrylate) (PMMA-OH) in the MTP process, and found that the resulting chemical patterns on replicas from all five blends were functional and able to direct the assembly of films of the same blends. The transfer temperature and the film annealing sequences had an impact on the MTP process. MTP was sensitive to the transfer temperature and could only be performed within a certain temperature range, *i.e.* higher than the glass transition temperature (T_g) of copolymers and lower than the rearrangement temperature of the assembled domains. Pre-organization of the blend films was also necessary for MTP since the preferential wetting of PMMA domains at the replica surface might result in the formation of a PMMA wetting layer to prevent the presentation of underlying chemical patterns to the replica surface.

Keywords Block copolymer; Molecular transfer printing; Thermal annealing; Chemical pattern; Directed self-assembly

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INTRODUCTION

Directed self-assembly of block copolymers has been demonstrated on chemical patterns to fabricate nanostructures with a variety of geometries and dimensions with high fidelity^[1, 2]. Currently, chemical patterns are fabricated by either 193 nm immersion lithography (193i) or electron beam lithography (EBL)^[3]. As the feature dimension continues to shrink, 193i has reached its optical limit and EBL suffers from low-throughput. It is critical to develop a new patterning technique for chemical patterns. Extreme ultra-violet interference lithography (EUV-IL) is a promising alternative to 193i or EBL, but it is still in the development stage and needs extremely high capital investment^[4]. Ji *et al.* developed a parallel patterning technique, molecular transfer printing (MTP), to create chemical patterns, including geometrically complex fingerprint patterns and device-oriented patterns, over macroscopic areas with feature dimensions below 15 nm^[5]. The MTP process used blends of polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA) block copolymers and functional homopolymer inks. Block copolymer domains served as reservoirs for inks, and homopolymer inks were segregated into their respective PS and PMMA domains in PS-*b*-PMMA block copolymers upon

annealing. During the MTP process, homopolymers were grafted or adsorbed on the replica substrate to create chemical patterns, replicating the domain structure present at the film surface^[5–7]. Jin *et al.* investigated the MTP by directed assembly of parallel cylindrical domains on topographic patterns^[8], while Liu *et al.* investigated the MTP of ternary blend films on sparse chemical patterns^[9]. In both of these combined processes, MTP could create chemical patterns with a higher feature density than the original lithographic pattern, which significantly reduced the patterning time and cost and overcame the resolution limit of current lithographic tools and materials. Furthermore, the domain dispersity can be improved by the MTP patterns. Thode *et al.* and Onses *et al.* demonstrated that they could print single homopolymer and backfill a second ink to functionalize the anchored brushes^[10, 11]. Onses *et al.* even transfer-printed a homopolymer ink with chemically different composition, PEG brushes, from PMMA domains of PS-*b*-PMMA films onto a second substrate^[12]. In addition, Inoue *et al.* developed an MTP strategy for patterning over large areas by a conformal layer-enhanced technique^[13].

In principle, MTP is compatible with the infrastructure in current microelectronics industry, and has high potential to reduce the production cost of chemical patterns, but there are still lots of process parameters that need to be explored to enable it a viable high-throughput technique. Herein we systematically studied the effects of molecular weights of

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homopolymers and transfer conditions on MTP in order to understand the process limit. We explored these parameters by (1) directing the assembly of the ternary blends on chemically nanopatterned substrates, (2) replicating the surface patterns of master films by MTP at different temperatures, and (3) comparing the re-assembled domain structures on replicas to original chemical patterns or surface domains in master films. We found that the molecular weights of homopolymer inks we used did not affect the transfer process, but the transfer conditions, *i.e.*, annealing temperatures and annealing sequences of films, were critical in order to faithfully replicate the surface domain pattern by MTP.

EXPERIMENTAL

Materials and Characterization

The block copolymer (PS-*b*-PMMA, $M_n = 52$ –52 kg·mol^{−1}) and homopolymers (PS-OH and PMMA-OH with various molecular weights) were purchased from Polymer Source, Inc. and had a polydispersity index of ~1.05–1.09. All solvents were purchased from Sigma-Aldrich and used as received.

Film thickness was measured with a spectroscopic ellipsometer (Sentech SE800). A Carl Zeiss Merlin field-emission scanning electron microscope (SEM) was used to image the block copolymer and ternary blend films using a 1 kV acceleration voltage.

The MTP Process

Chemically patterned substrates were fabricated on

6 kg·mol^{−1} PS-OH brushes by EUV-IL, as described in the literature^[5, 14]. Five lamellae-forming ternary blend films with ~50 nm thicknesses that contained 90 wt% PS-*b*-PMMA ($M_n = 52$ –52 kg·mol^{−1}), 5 wt% PS-OH and 5 wt% PMMA-OH were first assembled on chemical pattern at 190 °C. Then the MTP was performed at elevated temperatures for 24 h using those films as masters. After MTP, block copolymers and unreacted homopolymer inks were dissolved in chlorobenzene to recover the original master chemical patterns and generate replicas. The resulting replicas were subsequently used to direct the assembly of 50-nm-thick films of the corresponding blends at 190 °C.

RESULTS AND DISCUSSION

We used lamellae-forming ternary blends that contained 90 wt% PS-*b*-PMMA, 5 wt% PS-OH and 5 wt% PMMA-OH to explore these parameters for MTP. The molecular weights of PS-OH and PMMA-OH in the five blends ranged from 3.5 kg·mol^{−1} to 56 kg·mol^{−1} (Table 1). The periods of block copolymer-homopolymer ternary blends, L_B , increased with the increase of molecular weights of homopolymer inks^[15, 16]. L_B were calculated by fast Fourier transfer analysis of the SEM images of the perpendicularly oriented fingerprint structures from self-assembly of blend films on neutral brushes (Table 1)^[17–25], and the values agreed with those estimated from the empirical relationship reported by Liu *et al.*^[26].

A schematic and detailed description of the MTP process is shown in Fig. 1. We started with the preparation of MTP

Table 1 Compositions and blend periods of ternary blends with different molecular weight homopolymers (All blends contain 90 wt% of PS-*b*-PMMA, 5 wt% of PS-OH, and 5 wt% of PMMA-OH.)

Blend #	M_n of PS- <i>b</i> -PMMA (kg·mol ^{−1})	M_n of PS-OH (kg·mol ^{−1})	M_n of PMMA-OH (kg·mol ^{−1})	Blend period (L_B , nm)
Blend 3-3	52-52	3.7	3.5	49.6
Blend 6-6	52-52	6.0	6.0	50.3
Blend 10-9	52-52	10.2	9.5	51.4
Blend 20-24	52-52	20	24	52.3
Blend 51-56	52-52	51	56	54.0

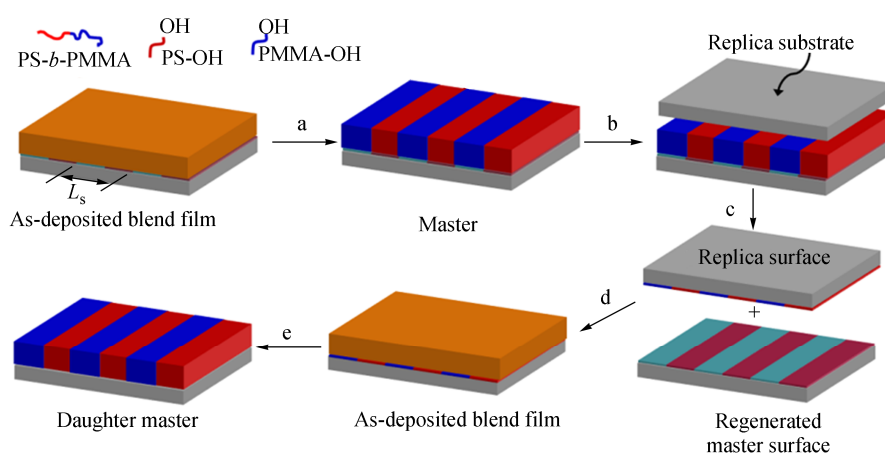


Fig. 1 Schematic of molecular transfer printing (MTP): (a) A ternary blend of PS-*b*-PMMA, PS-OH, and PMMA-OH is deposited as a film on a chemical pattern, and the blend film is annealed to form a master film. After DSA, homopolymers are sequestered into their respective domains; (b) A replica substrate is brought in contact with the surface of the assembled film. Homopolymers are transferred in the pattern of copolymer domains present at the master surface to create a chemical pattern of homopolymers on the replica; (c) Master and replica surfaces are separated by dissolving the block copolymer and ungrafted homopolymers in solvent to recover the patterned replica and the master surface (chemical pattern); (d) The same blend film is deposited on the replica surface and (e) assembled to create a daughter master

masters by directing the assembly of thin films of ternary blends on chemical patterns. Directed assembly of block copolymers (DSA of BCPs) on chemically patterned substrates has been realized with a high degree of perfection^[27–32]. We directed the assembly of five blend films (film thickness ~50 nm) with different pairs of homopolymers (as listed in Table 1) on chemical patterns with $L_s = 45$, 47.5 and 50 nm at 190 °C, where L_s is the period of line patterns^[33]. Figure 2(a) shows the surface morphologies of films imaged by SEM. Defect-free assembly, *i.e.* perpendicular domains were faithfully registered on underlying chemical patterns, of blends 3-3 ($L_B = 49.6$ nm) and 6-6 ($L_B = 50.3$ nm) was achieved on patterns with $L_s = 45$ –50 nm^[34, 35]. For blend 10-9 ($L_B = 51.4$ nm), defect-free DSA was only achieved on patterns with $L_s = 47.5$ and 50 nm, while guided assembly, *i.e.* partial registration of domains on underlying patterns, was obtained on patterns with $L_s = 45$ nm on which L_B is ~14% larger than L_s . The previous study already showed that defect-free assembly was only achieved on patterns with L_s s that deviated from L_o within 10%, where L_o is the natural

period of the block copolymer, and defects would form on patterns if the difference between L_s and L_o was larger than 10%, in agreement with our observation. Further increase of the molecular weights of homopolymers led to even larger L_B s for blends 20-24 ($L_B = 52.3$ nm) and 51-56 ($L_B = 54.0$ nm). As a result, defect-free assembly was only realized on chemical patterns with $L_s = 50$ nm for these two blends. Partially aligned domains with defects, *e.g.* dislocation of domains, were found on patterns with $L_s = 47.5$ nm. For these two blends, L_B s were ~10.1% and 13.6% larger than L_s , respectively. Again, these observations agreed with the previous study^[35]. On patterns with $L_s = 45$ nm, the difference between L_s and L_B was larger than 16%. The domains were no longer registered with the underlying patterns and only fingerprint structures formed for both blends.

Previously, Ji *et al.* demonstrated that MTP allowed for the transfer of well-defined patterns with high fidelity, and the resulting brushes on replicas exactly mirrored to original surface domain patterns of masters^[5]. After DSA, the domain patterns in block copolymer films were exactly the same as

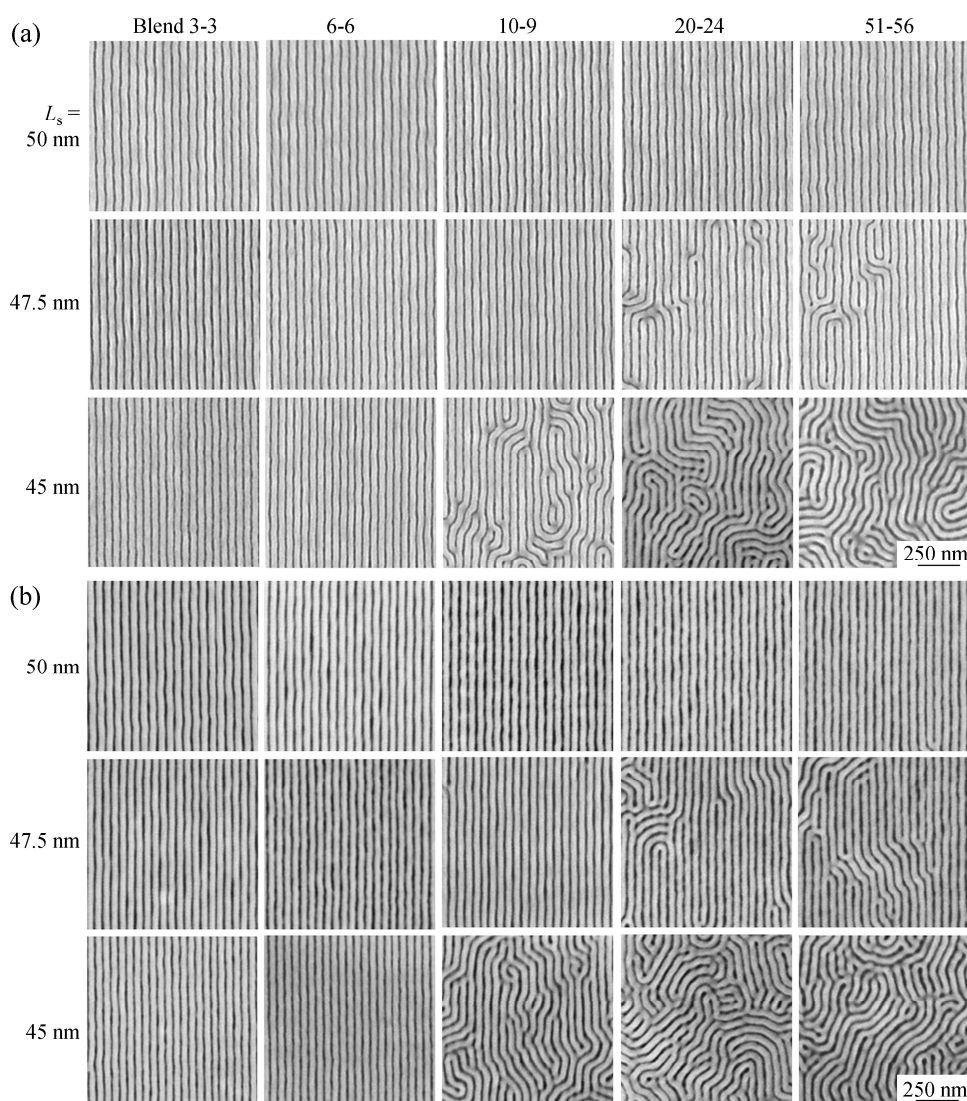


Fig. 2 SEM images of five different blend films assembled at 190 °C for 24 h on (a) chemical patterns with $L_s = 45$, 47.5, and 50 nm fabricated by EUV-IL and (b) their respective MTP replicas

the brush patterns on replicas. Due to the known difficulty of imaging the thin brush layer, we, instead, imaged the re-assembled films on replicas to examine the transfer quality. We performed MTP at 160 °C for 24 h using those five blend films as masters. During thermal annealing, homopolymer inks were grafted to the replica surfaces through the dehydration reaction between the hydroxyl groups on homopolymer chain ends and the native silicon oxide on replica surfaces. After MTP, block copolymers and unreacted homopolymer inks were dissolved in chlorobenzene to recover the original master chemical patterns and generate replicas. The resulting replicas were subsequently used to direct the assembly of 50-nm-thick films of the corresponding blends at 190 °C. Figure 2(b) shows the SEM images of the assembled films. The assembly behaviors of blend films on these replicas were similar to those on their corresponding original chemical patterns. Defect-free assembly was only achieved at regions on the MTP replicas that were complementary to regions without defects on masters in Fig. 2(a). For those regions that master patterns had defects, similar guided assembly or fingerprint structures were also obtained on MTP replicas (Fig. 2b). Therefore, the molecular weights of homopolymer inks did not affect the transfer process, and inks could be effectively transferred to and grafted onto the replica substrates following the surface domain patterns of the assembled films.

The printing temperature had a significant impact on the MTP process. MTP was tested at 130–230 °C with a 10 °C increment for 24 h from 50-nm-thick blend 6-6 and blend 51-56 films that were directed to assemble on chemical patterns with $L_s = 50$ nm. We roughly estimated the diffusion coefficient of 6 and 56 kg·mol⁻¹ PS at 130 °C to be $\sim 10^{-14}$ and $\sim 10^{-13}$ cm²·s⁻¹, respectively^[36]. At such temperature, it only took a couple of minutes for inks to diffuse across the 50-nm-thick films to the replica substrate. Diffusion of inks within domains was not the limiting factor for the brush grafting under these annealing temperatures. After MTP, blend 6-6 films were deposited on the replica surfaces and annealed at 190 °C for 24 h. Defect-free assembly was achieved on replicas that were generated by MTP at 130–220 °C. Figure 3 shows the representative SEM images

of blend 6-6 films assembled on the MTP replicas that were fabricated at 190–220 °C. However, a mixture of broken fingerprint structures and parallel structures was observed on the replica created by MTP at 230 °C (Fig. 4). The master may rearrange to form parallel domains at the preferential wetting replica surface in a time frame shorter than reaction of the inks with the surface at 230 °C, leading to the formation of a preferential brush layer instead of stripped chemical patterns on the replica. We did not perform MTP at temperatures close to or below the glass transition temperature of PS-*b*-PMMA due to the limited diffusivity of inks.

Pre-ordering of the blend film is necessary for the MTP process. We chose 220 °C as the printing temperature using the as-spun film as the master films because MTP can be performed at this temperature and DSA of BCP films on chemical patterns could reach equilibrium within 5 min at 220 °C^[37]. If the driving force provided by the underlying substrate is much larger than the preferential wetting of PMMA on the top replica surface, a perpendicular orientation of lamellar domains may form even in presence of a preferential top surface. If this is true, it may provide an opportunity to assemble the master film and subsequently transfer the pattern in one annealing step. To test this hypothesis, blend 6-6 films were spin-coated on chemical patterns with $L_s = 50$ nm fabricated by EUV-IL. After MTP from these as-spun films at 220 °C, the replicas were used to direct the assembly of blend 6-6 films at 190 °C. The patterned areas were easily located on the replicas and imaged by SEM; however, no aligned block copolymer domains but a mixture of broken fingerprint and parallel structures were observed on all replicas, similar to the images in Fig. 4. This meant that the brush patterns on replicas did not mirror the original chemical patterns on master substrates. The nucleation of domains may occur independently from both interfaces during annealing, and the equilibrium structure, *i.e.* a mixed structure of parallel lamellae near the replica surface and perpendicular lamellae near the EUV patterned substrate, may form in a time frame shorter than the time needed for the brush grafting.

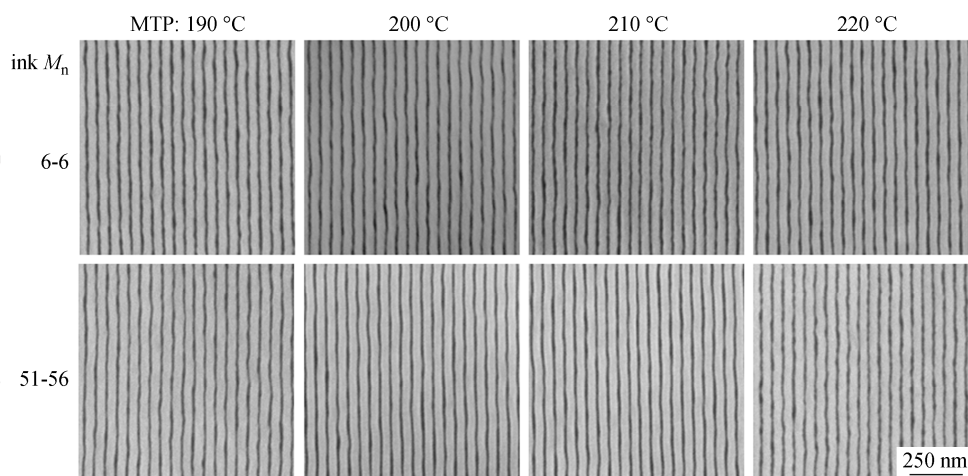


Fig. 3 SEM images of the 50-nm-thick blend 6-6 films assembled on the replicas generated by MTP at 190–220 °C with different pairs of inks (6-6 and 51-56)

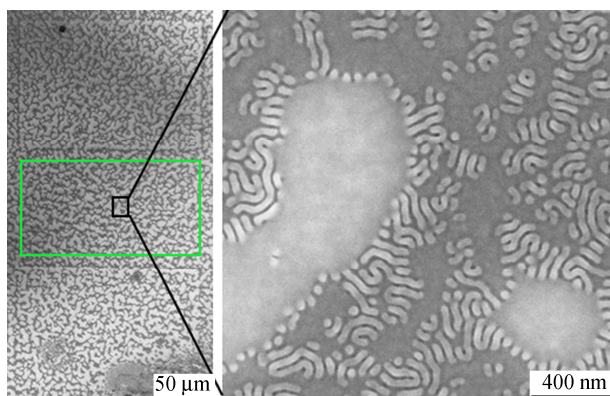


Fig. 4 SEM images of a 50-nm-thick blend 6-6 film assembled on the replica generated by MTP at 230 °C (The EUV-IL patterned area was highlighted by the green rectangle, and the high-magnification image (right) was taken within the patterned area)

CONCLUSIONS

In summary, we demonstrated that MTP could be successfully performed using homopolymer inks with a large range of molecular weights ($M_n \sim 3.5\text{--}56 \text{ kg}\cdot\text{mol}^{-1}$), and the molecular weights of homopolymer inks did not affect the MTP process. MTP could only be performed within a certain temperature range, *i.e.* higher than T_g of copolymers and lower than the rearrangement temperature of the assembled domains. Pre-organization of the blend films is necessary for MTP since the wetting layer of PMMA domains at the replica surface may prevent the presentation of underlying chemical patterns to the replica surface.

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