Published in final edited form as:

Chem Sci. 2013 May 1; 4(5): 2093–2099. doi:10.1039/C3SC50423A.

The role of viscosity on polymer ink transport in dip-pen nanolithography

Guoliang Liu^{a,†}, Yu Zhou^{b,†}, Resham S. Banga^c, Radha Boya^a, Keith A. Brown^a, Anthony J. Chipre^a, SonBinh T. Nguyen^a, and Chad A. Mirkin^{a,b,c,*}

^aDepartment of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208 USA.

^bDepartment of Materials Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208 USA.

^cDepartment of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208 USA.

Abstract

Understanding how ink transfers to a surface in dip-pen nanolithography (DPN) is crucial for designing new ink materials and developing the processes to pattern them. Herein, we investigate the transport of block copolymer inks with varying viscosities, from an atomic force microscope (AFM) tip to a substrate. The size of the patterned block copolymer features was determined to increase with dwell time and decrease with ink viscosity. A mass transfer model is proposed to describe this behaviour, which is fundamentally different from small molecule transport mechanisms due to entanglement of the polymeric chains. The fundamental understanding developed here provides mechanistic insight into the transport of large polymer molecules, and highlights the importance of ink viscosity in controlling the DPN process. Given the ubiquity of polymeric materials in semiconducting nanofabrication, organic electronics, and bioengineering applications, this study could provide an avenue for DPN to expand its role in these fields.

Introduction

Dip-pen nanolithography (DPN), originally developed as a molecular patterning technique for printing small alkanethiol molecules on an Au surface,¹ has rapidly become a versatile tool for making nanostructures on many types of surfaces from a wide variety of materials such as sols,² nanoparticles,^{3–5} nucleic acids,⁶ proteins,^{7, 8} phospholipids,⁹ collagen,¹⁰ metallomesogens,¹¹ and bacteria.¹² Such capabilities have enabled important new applications in chemistry, materials science, and biology.^{13–21} Recent additions to the arsenal of DPN inks are block copolymers loaded with metal salts, which, when patterned, can be subsequently reduced to generate individual crystalline nanoparticles through a technique termed scanning probe block copolymer lithography (SPBCL).²² Initially, this technique was limited to a few highly mobile materials such as Au and CdS,^{22, 23} but research into the mechanism underlying particle formation has led to a step-wise annealing process that has generalized the method for a large class of nanostructures, including many metals, metal oxides, and metal alloys.²⁴ However, the mechanistic factors that underlie

This journal is © The Royal Society of Chemistry

chadnano@northwestern.edu.

[†]These authors contribute equally to this work.

[†]Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

block copolymer ink transfer from tip to surface during SPBCL have yet to be elucidated. Given the importance of this step, a fundamental investigation of the ink transfer process is critical for a comprehensive understanding of the entire nanoparticle synthetic method, as well as the design of new inks for broader applications.

Previous mechanistic studies into the DPN process have focused extensively on the transfer of small molecules that form self-assembled monolayers.^{25–36} A diffusion model in which the ink molecules diffuse from the tip to the surface can explain the meniscus-mediated transfer and patterning of such conventional ink molecules. According to this model, the diameter of a patterned feature scales linearly with the square root of time that the tip spends in contact with the surface at the patterning location, known as the dwell time.²⁵ There are two important assumptions in this model: 1) the ink molecules diffuse on the substrate from a point source that has a given molecular flow rate, and 2) the ink molecules are so small that they can diffuse independently and follow a random-walk motion before chemisorption onto the substrate. These assumptions are valid for small molecules such as 16-mercaptohexadecanoic acid (MHA) or 1-octadecanethiol (ODT).²⁵ In contrast, the block copolymers used in SPBCL have significantly larger molecular weights,²⁴ and importantly, these chain-like polymer molecules are entangled with one another at the nanometer scale such that they cannot diffuse independently.³⁷ As a result, the assumption of independent molecular diffusion is not valid, and thus the model is not applicable to block copolymer ink transfer. While chemisorption of the molecules on the surface is a driving force for the transfer of small molecules, block polymer molecules are physisorbed onto surfaces. Therefore, a different transport behaviour is expected for this class of materials, leading to questions such as, how are polymer inks transferred from the AFM tip to the substrate, and which parameters govern the transfer of polymer inks from tip to substrate? Examples of patterning polymer melts using thermal DPN have revealed that polymer flow is affected by ink viscosity,²⁶ yet for aqueous polymer solution transport *via* DPN, the effect of viscosity on the ink flow during the patterning process is unknown.

Results and Discussion

To develop a working mechanism of polymer ink transfer from an AFM tip to a substrate, we first experimentally investigated the patterning of polymer inks with differing viscosities. In the SPBCL process, a block copolymer ink that has been loaded with a metal precursor is deposited onto a surface, and then thermally annealed to remove the polymer matrix while converting the metal precursor into a single nanoparticle.²⁴ Interestingly, the ink used in the SPBCL process provides a simple way of tuning the polymer ink viscosity, in that the ink viscosity is directly related to the amount of loaded metal precursor.³⁸ In a typical experiment, the block copolymer poly(ethylene oxide)-*block*-poly(2-vinyl pyridine) (PEO-*b*-P2VP, $M_n=2.8\text{--}1.5\text{ kg}\cdot\text{mol}^{-1}$) was mixed with the metal salt HAuCl_4 . Inks with different viscosities were prepared by varying the amount of Au loading in the block copolymer ink (α), which is defined as the molar ratio between Au and 2-vinyl pyridine in the block copolymer ($\alpha = [\text{Au}]:[\text{2VP}]$). In this work, the inks have Au loadings of $\alpha=1:4$, $1:8$, $1:16$, $1:32$, and $1:64$. After dissolution of the loaded polymer in water at concentrations above its critical micelle concentration, the block copolymer assembles into micelles (Fig. S1).^{38, 39}

We observed that the ink viscosity depends strongly on Au loading (Fig. 1). For the block copolymer ink with an Au loading of $\alpha=1:64$ and a polymer concentration of $200\text{ mg}\cdot\text{ml}^{-1}$, the ink is slightly shear thinning and the viscosity plateaus at a shear rate of $\sim 10\text{ s}^{-1}$ (Fig. 1 inset). Importantly, the fact that this ink is shear thinning highlights the inability of the polymer to move independently, supporting the argument that polymeric inks deviate from the conventional molecular diffusion model of DPN transport. To extract viscosity values

for comparison, we use the values of the viscosity in the regime where they are independent of shear rate (example in Fig. 1 inset, plateau region). In this regime, the viscosity of the block copolymer ink increases from 27.0 to 45.8 mPa·s as α increases from 1:64 to 1:4 (Fig. 1, bottom panel). As a result of the relatively low molecular weight, the block copolymer forms loose micelles, which interact with one another through weakly intercalated block copolymer molecules.³⁸ Increasing the amount of HAuCl₄ enhances the strength of the interactions between the micelles via coordination of Au with multiple pyridine groups from different polymer chains,^{38, 40} resulting in an increased ink viscosity. Indeed, it is remarkable that the ink viscosity increases 70% by increasing the Au loading in the block copolymer from 1:64 to 1:4.

Block copolymer inks with different viscosities behave differently during patterning. Using DPN, the aforementioned polymer inks were patterned on hydrophobic silicon substrates to generate nanoreactors for synthesizing nanoparticles; feature volume was controlled by varying dwell time (Fig. 2). The patterned block copolymer feature sizes (both diameter and volume) were quantified by AFM and plotted as a function of dwell time (Fig. 3). In general, the block copolymer feature size increased with increasing dwell time and decreasing ink viscosity. From 0.01 to 1 s, the patterned block copolymer feature size increased rapidly, but exhibited a markedly decreased rate of growth from 1 to 10 s. When α was decreased from 1:4 to 1:16, the feature size was significantly increased for a given dwell time (for example, 0.01 s in Fig. S2). Increasing α further to 1:32 and 1:64 did not yield appreciably faster rates of deposition, likely because the viscosities of the polymer inks were comparable in this range (Fig. 1). It is also important to note that neither the feature diameter or volume scales linearly with the square root of time over the entire dwell time range, confirming that the conventional molecular diffusion model²⁵ is not applicable to these inks.

To describe the observed behavior of polymer ink transfer from an AFM tip to a substrate, we propose a mass transfer model to calculate the amount of ink that transports across any horizontal cross-section near the end of the AFM tip (Fig. 4a and b). For simplicity, we adopt a cylindrical approximation of an AFM tip that has a tip radius of R_1 .²⁶ In this model, the tip was coated with a polymer layer, and we assume that the thickness of this ink layer does not change during an experiment, as there is a reservoir of ink on the cantilever at the top of the AFM tip. We define the thickness of polymer ink as $R_2 - R_1$. For simplicity, we assume the water-based ink used here is nearly a Newtonian fluid under our patterning conditions. Given that inertial effects are negligible because of the extremely low Reynolds number in this system,²⁶ the polymer velocity profile on the AFM tip can be approximated by the Stokes equations,

$$0 = -\nabla p + \mu \nabla^2 v + \rho g \quad (1)$$

where v , ∇p , μ , ρ and g are, respectively, velocity of ink flow, pressure gradient along the tip, ink viscosity, ink density, and gravity. Since there is no radial or angular flow ($v_r = 0$ and $v_\phi = 0$), the equation can be simplified to,

$$\nabla^2 v_z = \frac{F}{\mu} \quad (2)$$

where $F = \rho g - \nabla p$. Because the thicknesses of ink coating on the tip are similar between different inks, the cross-sectional area does not change much. Since the final volume of polymer ink that is delivered onto the substrate is an integration of ink velocity with respect to time and cross-sectional area, it should also be inversely proportional to the ink viscosity. In addition, the pressure gradient ∇p depends upon the surface energy of the ink materials, as well as the shape of the polymer features on the substrate. As shown in previous work,²⁶

the pressure gradient is proportional to the curvature difference between the polymers at the top and bottom of the tip. The curvature of polymer at the top of the tip is zero, and at the bottom the curvature is determined by the polymer feature size whose curvature decreases with dwell time. Based on this model, we expect that: 1) given the same dwell time, a more viscous ink results in smaller patterned polymer features; 2) given the same ink viscosity, the volume of the patterned features increases with dwell time, but the ink transfer rate decreases with dwell time. The projected profile of polymer volume as a function of dwell time and viscosity is schematically shown in Fig. 4d. Indeed, our measured data confirm that the relationships between the volume of polymer features, dwell time, and ink viscosity (Fig. 3) are in agreement with the mass transfer model. The final shape and diameter of the deposited polymer features, however, are determined by the interfacial energies between air, polymer and the substrate.

We further explored the utility of these polymer features to synthesize single nanoparticles of various sizes by analyzing the size of the nanoparticles as a function of polymer feature size. Following the protocol of SPBCL synthesis of nanoparticles,²⁴ the patterned block copolymer features were annealed stepwise at 150 °C for 4 h and at 500 °C for 4 h under an Ar atmosphere. An SEM image of an array of Au nanoparticles formed from a block copolymer ink with an Au loading $\alpha = 1:4$ confirms that the size of the synthesized nanoparticles increases with dwell time (Fig. 5).

The nanoparticle size is a function of the polymer feature size and the metal salt concentration (Fig. 6). We found that for patterned polymer features with the same diameter, the size of the nanoparticles increases as the Au loading increases. In principle, the nanoparticle size should be governed by the number of Au atoms, $N_{Au\ atom}$ in the patterned block copolymer nanoreactor or in the synthesized nanoparticle,

$$N_{Au\ atom} = \frac{\rho_p V_p}{M_{w,p}} N_A N_{2VP} \alpha = \frac{\rho_g V_g}{M_{w,g}} N_A \quad (3)$$

in which ρ , V , M_w , N_A , N_{2VP} are density, volume, molecular weight, Avogadro number, and number of 2VP monomers in one block copolymer chain, respectively. The subscripts p and g denote polymer and gold nanoparticle, respectively. Since $V_p \propto D^3$, and $V_g \propto d^3$, where D and d are the diameters of the polymer feature and nanoparticles, the diameters of the nanoparticle and the block copolymer feature should be related by the proportionality,

$$d/D \propto \sqrt[3]{\alpha} \quad (4)$$

Therefore, we linearly fit the diameter of nanoparticle with respect to the diameter of the block copolymer features and the slopes of the fitted lines follow the above scaling law (Fig. 6).

Conclusions

We have found that viscosity plays a major role in polymer ink transfer during DPN. A slight increase of Au loading in the block copolymer increases the ink viscosity, giving it vastly different transfer properties during patterning. A mass transport model was developed to describe the patterning of block copolymer inks. In contrast with the conventional small molecule diffusion model, in which the small molecule ink transfer is governed by diffusivity, the mass transport model here highlights viscosity as an important parameter to control the patterning of large molecule inks. It should be noted that, to generalize this model to other compositions of inks, there are two other physical parameters which must be considered and were assumed to be fixed in this study. The first is the interfacial energy

between the ink and the surface, which is believed to provide the driving force for transport. The second is the thickness of the ink layer on the wall of the tip. Comparing different ink materials or coating conditions will require a more detailed treatment of how this thickness is affected by these parameters. Qualitatively, however, this model is expected to explain the behavior of all inks, including different molecular weight polymers, that behave as viscous liquids. The patterned block copolymer features can act as nanoreactors for nanoparticle synthesis. The extracted relationships between nanoparticle size and both dwell time and metal salt loading serve as guidelines for synthesizing nanoparticles with desired sizes on a surface, which are important for applications in catalysis, plasmonics, and nanolithography. Given that viscosity is a generic material property, this study should also offer insight into patterning other advanced materials for the assembly of a wide variety of nanostructures.^{12, 41–45}

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This material is based upon work supported by DARPA/MTO Award N66001-08-1-2044, AOARD Award FA2386-10-1-4065, AFOSR Award FA9550-12-1-0141, NSF Awards DBI-1152139 and DMB-1124131, DoD/NPS/NSSEF Fellowship Awards N00244-09-1-0012 and N00244-09-1-0071, UOP-Honeywell, Chicago Biomedical Consortium with support from Searle Funds at The Chicago Community Trust, and NERC an Energy Frontier Research Center funded by the DoE/ Office of Science/Office of Basic Energy Sciences Award DE-SC0000989. R.B. acknowledges the Indo-US Science & Technology Forum (IUSSTF) for a postdoctoral fellowship. K.A.B. gratefully acknowledges support from the Northwestern University's International Institute for Nanotechnology. R.S.B. and A.J.C. are partially supported by the NIH (NCI CCNE Grant C54CA151880). A.J.C. is partially supported by the AFOSR (agreement FA-9550-11-1-0275). The authors thank the Northwestern University Electron Probe Instrumentation Center (EPIC). Any opinions, findings, and conclusions or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the sponsors.

Notes and References

1. Piner RD, Zhu J, Xu F, Hong SH, Mirkin CA. *Science*. 1999; 283:661–663. [PubMed: 9924019]
2. Su M, Liu X, Li S-Y, Dravid VP, Mirkin CA. *J. Am. Chem. Soc.* 2002; 124:1560–1561. [PubMed: 11853414]
3. Liu X, Fu L, Hong S, Dravid VP, Mirkin CA. *Adv. Mater.* 2002; 14:231–234.
4. Wang WM, Stoltenberg RM, Liu S, Bao Z. *ACS Nano*. 2008; 2:2135–2142. [PubMed: 19206460]
5. Li B, Goh CF, Zhou X, Lu G, Tantang H, Chen Y, Xue C, Boey FYC, Zhang H. *Adv. Mater.* 2008; 20:4873–4878.
6. Demers LM, Ginger DS, Park S-J, Li Z, Chung S-W, Mirkin CA. *Science*. 2002; 296:1836–1838. [PubMed: 12052950]
7. Lee K-B, Lim J-H, Mirkin CA. *J. Am. Chem. Soc.* 2003; 125:5588–5589. [PubMed: 12733870]
8. Zhou X, Chen Y, Li B, Lu G, Boey FYC, Ma J, Zhang H. *Small*. 2008; 4:1324–1328. [PubMed: 18712751]
9. Lenhart S, Sun P, Wang Y, Fuchs H, Mirkin CA. *Small*. 2007; 3:71–75. [PubMed: 17294472]
10. Wilson DL, Martin R, Hong S, Cronin-Golomb M, Mirkin CA, Kaplan DL. *Proc. Natl. Acad. Sci. USA*. 2001; 98:13660–13664. [PubMed: 11707577]
11. Radha B, Liu G, Eichelsdoerfer DJ, Kulkarni GU, Mirkin CA. *ACS Nano*. 2013
12. Kim J, Shin Y-H, Yun S-H, Choi D-S, Nam J-H, Kim SR, Moon S-K, Chung BH, Lee J-H, Kim J-H, Kim K-Y, Kim K-M, Lim J-H. *J. Am. Chem. Soc.* 2012; 134:16500–16503. [PubMed: 22992015]
13. Salaita K, Wang Y, Mirkin CA. *Nature Nanotech.* 2007; 2:145–155.

14. Torrey JD, Vasko SE, Kapetanovic A, Zhu ZH, Scholl A, Rolandi M. *Adv. Mater.* 2010; 22:4639–4642. [PubMed: 20872407]
15. Saavedra HM, Mullen TJ, Zhang PP, Dewey DC, Claridge SA, Weiss PS. *Rep. Prog. Phys.* 2010; 73:036501.
16. Unruh DA, Mauldin C, Pastine SJ, Rolandi M, Fréchet JMJ. *J. Am. Chem. Soc.* 2010; 132:6890–6891. [PubMed: 20438114]
17. Oberhansl S, Hirtz M, Lagunas A, Eritja R, Martinez E, Fuchs H, Samitier J. *Small.* 2012; 8:541–545. [PubMed: 22258752]
18. Sekula-Neuner S, Maier J, Oppong E, Cato ACB, Hirtz M, Fuchs H. *Small.* 2012; 8:585–591. [PubMed: 22278752]
19. Zhou X, Boey F, Zhang H. *Chem. Soc. Rev.* 2011; 40:5221–5231. [PubMed: 21713267]
20. Zhou X, Boey F, Huo F, Huang L, Zhang H. *Small.* 2011; 7:2273–2289.
21. Ginger DS, Zhang H, Mirkin CA. *Angew. Chem. Int. Ed.* 2004; 43:30–45.
22. Chai J, Huo F, Zheng Z, Giam LR, Shim W, Mirkin CA. *Proc. Natl. Acad. Sci. USA.* 2010; 107:20202–20206. [PubMed: 21059942]
23. Giam LR, He S, Horwitz NE, Eichelsdoerfer DJ, Chai J, Zheng Z, Kim D, Shim W, Mirkin CA. *Nano Lett.* 2012; 12:1022–1025. [PubMed: 22250864]
24. Liu G, Eichelsdoerfer DJ, Rasin B, Zhou Y, Brown KA, Liao X, Mirkin CA. *Proc. Natl. Acad. Sci. USA.* 2013; 110:887–891. [PubMed: 23277538]
25. Jang JY, Hong SH, Schatz GC, Ratner MA. *J. Chem. Phys.* 2001; 115:2721–2729.
26. Felts JR, Somnath S, Ewoldt RH, King WP. *Nanotechnology.* 2012; 23:215301. [PubMed: 22551550]
27. Wu CD, Fang TH, Wu TT. *Polymer.* 2012; 53:857–863.
28. Wu CD, Fang TH, Lin JF. *J. Colloid Interface Sci.* 2011; 361:316–320. [PubMed: 21658704]
29. Saha SK, Culpepper ML. *Appl. Phys. Lett.* 2010; 96:243105.
30. Saha SK, Culpepper ML. *J. Phys. Chem. C.* 2010; 114:15364–15369.
31. Kim H, Saha LC, Saha JK, Jang J. *Scanning.* 2010; 32:2–8. [PubMed: 19787663]
32. Sheehan PE, Whitman LJ. *Phys. Rev. Lett.* 2002; 88:156104. [PubMed: 11955210]
33. John NS, Kulkarni GU. *J. Nanosci. Nanotechnol.* 2007; 7:977–981. [PubMed: 17450862]
34. Weeks BL, Vaughn MW, DeYoreo JJ. *Langmuir.* 2005; 21:8096–8098. [PubMed: 16114907]
35. Wu TH, Lu HH, Lin CW. *Langmuir.* 2012; 28:14509–14513. [PubMed: 23020585]
36. Zeira A, Chowdhury D, Hoepfner S, Liu S, Berson J, Cohen SR, Maoz R, Sagiv J. *Langmuir.* 2009; 25:13984–14001. [PubMed: 19835384]
37. de Gennes PG, Leger L. *Annu. Rev. Phys. Chem.* 1982; 33:49–61.
38. Bronstein LM, Sidorov SN, Valetsky PM, Hartmann J, Cölfen H, Antonietti M. *Langmuir.* 1999; 15:6256–6262.
39. Martin TJ, Procházka K, Munk P, Webber SE. *Macromolecules.* 1996; 29:6071–6073.
40. Barakat K, Cundari TR. *Chem. Phys.* 2005; 311:3–11.
41. Chen T, Amin I, Jordan R. *Chem. Soc. Rev.* 2012; 41:3280–3296. [PubMed: 22234473]
42. Liu GL, Ramirez-Hernandez A, Yoshida H, Nygard K, Satapathy DK, Bunk O, de Pablo JJ, Nealey PF. *Phys. Rev. Lett.* 2012; 108:065502. [PubMed: 22401084]
43. Liu GL, Thomas CS, Craig GSW, Nealey PF. *Adv. Funct. Mater.* 2010; 20:1251–1257.
44. Nakashima H, Higgins MJ, O'Connell C, Torimitsu K, Wallace GG. *Langmuir.* 2012; 28:804–811. [PubMed: 22103712]
45. Zhou XC, Liu ZL, Xie Z, Liu XQ, Zheng ZJ. *Small.* 2012; 8:3568–3572. [PubMed: 22887938]

Fig. 1. (top) Shear stress as a function of shear rate for block copolymer inks with different Au loadings α . (bottom) Viscosity of polymer inks as a function of Au loading. The ink viscosity almost doubles as the Au loading increases from 1:64 to 1:4. (inset) Example of a viscosity measurement for the block copolymer ink with $\alpha = 1:64$. The viscosity reaches a plateau at high shear rates.

Fig. 2. AFM height images of the patterned polymer features from different inks. The Au loading, α , varies from 1:4 to 1:64, and the patterning dwell time ranges from 0.01 to 10 s. The dwell time sequence and scale bars apply to all AFM images.

Fig. 3. (a, b) Diameter and (c, d) volume of patterned polymer features as a function of dwell time and Au loading. (b) and (d) are expanded views of (a) and (c) at lower dwell times, respectively. The lines in (a) and (b) are a guide to the eye, and those in (c) and (d) are fitted lines (see ESI).

Fig. 4. Schematic of mass transfer during DPN patterning of an aqueous polymer ink. (a) An AFM tip with defined cylindrical coordinates. (b) Profile of the ink velocity (v) across a horizontal thin slab. The tip diameter is R_1 , and the thickness of polymer ink layer is $R_2 - R_1$. (c) The polymer ink transfers from the tip to a hydrophobic substrate through a meniscus. (d) The final volume (V) of the patterned polymer features as a function of dwell time (t) and ink viscosity (μ).

Fig. 5. SEM image of nanoparticles synthesized within patterned polymer nanoreactors with various dwell times. The Au loading α in the ink is 1:4. The dwell time follows the same sequence as that in Fig 3. For clarity, only the first two dwell times are shown.

Fig. 6. The scaling behaviour of nanoparticle size. (a) Diameter of Au nanoparticles in polymer nanoreactors. The nanoparticle size scales linearly with the size of polymer nanoreactors. (b) The slope (β) of the fitted lines in (a) scales linearly with $\sqrt[3]{\alpha}$.