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

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## Supporting Information

### Experimental Section

**Materials.** Poly(ethylene oxide)-*block*-poly(2-vinyl pyridine) (PEO-*b*-P2VP, $M_n$=2.8-*b*-1.5 kg•mol$^{-1}$, polydispersity index, PDI=1.11) was purchased from Polymer Source, Inc. and used as received. Tetrachloroauric(III) acid trihydrate ($HAuCl_4{\cdot}3H_2O$), hexamethyldisilazane (HMDS) and hexane were purchased from Sigma-Aldrich, Inc., and used as received. DPN® pen arrays (Type M, no gold-coating) were purchased from Nanoink, Inc. Silicon wafers were purchased from Nova Electronic Materials.

**Sample Preparation.** PEO-*b*-P2VP and $HAuCl_4{\cdot}3H_2O$ were dissolved in water, and then mixed with a controlled molar ratio between 2VP and Au from 4 to 64. The final ink had a PEO-*b*-P2VP concentration of 5 mg·ml$^{-1}$. After stirring overnight, the solution was dip-coated onto a DPN pen array. After drying in an $N_2$ stream, the pen array was mounted onto an AFM (NScriptor, NanoInk, Inc.) in a chamber with controlled humidity. The relative humidity was in the range of 85%. Prior to DPN patterning, the silicon wafers were kept in a desiccator with two vials of HMDS and hexane mixture for 24 h to ensure that they were hydrophobic.

The patterned substrate was placed in a tube furnace. The annealing conditions were programed as follows: ramp to 150 °C in 1 h, soak at 150 °C for 4 h in Ar, cool down to room temperature in 1 h, ramp to 500 °C in 1 h, soak at 500 $^{o}$C for 4 h in Ar, cool down to room temperature in 1 h.

### Characterization.

**Dynamic light scattering (DLS).** The hydrodynamic radius of Au loaded block copolymer micelles were measured on a Malvern Zetasizer at room temperature.

**Rheometry.** To approximate the block copolymer inks on the AFM tips during patterning, we measured the viscosity for inks with a relatively high concentration (200 mg·ml$^{-1}$). Viscosities of the polymer inks were measured on a Paar Physica MCR300 viscometer at room temperature. To approximate the conditions at the tip during patterning, the ink concentration used for the viscosity measurement was 200 mg·ml$^{-1}$.

**Atomic force microscopy (AFM).** The patterned polymer features were analyzed on a Bruker dimension icon with ScanAsyst. The height profiles were exported from Nanoscope. The diameter and height of the polymer nanoreactors were measured directly, and the volume was calculated by integrating the height over area that each polymer nanoreactor spans.

**Scanning electron microscopy (SEM).** The final nanoparticle size was characterized with a Hitachi S-4800 SEM at an acceleration voltage of 5 kV and a current of 20 μA. Probe current was set to high, and focus mode was set to ultrahigh resolution (UHR). Only the upper second electron detector was used. The measured sizes of nanoparticles were compared and calibrated with those measured with TEM.

**Scanning transmission electron microscopy (STEM).** Hitachi STEM HD-2300A in Z-contrast mode at an acceleration voltage of 200 kV and a current of 78 μA was used to calibrate the size measurement of nanoparticles by SEM. The samples for calibration were patterned on 50-nm-thick hydrophobic silicon nitride membranes.

## Polymer feature size fitting

In order to explore the fundamental relationship between the polymer transport dynamics and the viscosity of the ink, analysis of the measured volume data was performed. To enable quantitative comparison of the data, the volume for each ink concentration was fit to the phenomenological function,

$$V = \frac{V_0(t + t_0)}{(t + t_0) + \tau}, \tag{S1}$$

using a least-squares fit (Fig. S3). Despite the phenomenological nature of this function, the fitting parameters $V_0$, $t_0$, and $\tau$ can be physically interpreted as a maximum volume, an offset time, and a saturation time scale, respectively. The offset time is assumed to represent the unavoidable contact time added to the dwell time by the finite time it takes the instrument to reach the force set point once in contact with the surface. This interpretation of this parameter enforces the condition that for a true contact time approaching 0, there should be no volume of polymer deposited. Consistent with this prediction, the offset time is found to be uncorrelated to the viscosity (Fig. S4), in agreement with this being a random experimental parameter. It is worth noting that the data point representing $\alpha = 1:8$ is the only data point not within 5 ms of 60 ms. More interestingly, the maximum feature size clearly depends on viscosity and a linear trend provides an excellent fit between these parameters (Fig. S5). Finally, the saturation time displays a weak correlation with viscosity, thrown off largely by the 1:8 data, suggesting a relationship between the dynamics of patterned spot formation and the viscosity of the ink. Taking the previously described model of low-Reynolds number pressure driven flow in which,

$$\frac{dV}{dt} \propto \frac{F}{\mu}, \tag{S2}$$

we can conclude that in this model, the driving force is initially proportional to $\frac{\mu V_0}{\tau}$, and decays steadily to 0 as time progresses. When this value is plotted for the five inks here, $\frac{\mu V_0}{\tau}$ is found to depend very strongly on viscosity, changing nearly an order of magnitude as the viscosity less than doubles; the power law of the fit is -3.7 (Fig. S7). These empirical relationships imply that through control over the viscosity of a given ink, it may be possible to tune the maximum feature size and rate of transport of a given ink.

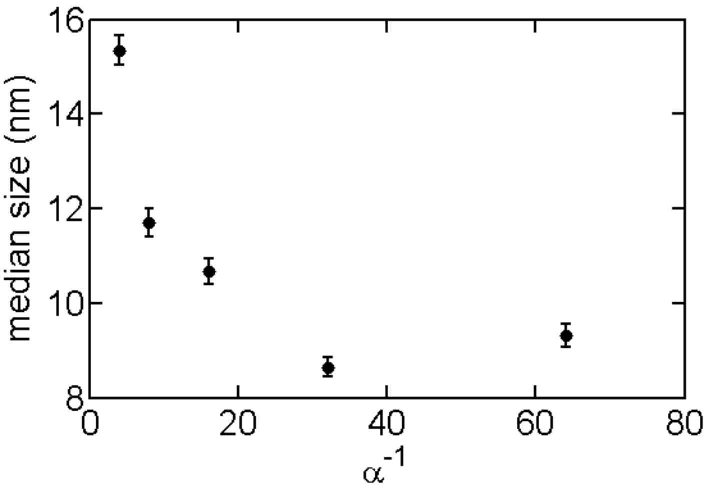

**Figure S1.** Hydrodynamic diameter of the block copolymer micelles measured by dynamic light scattering.

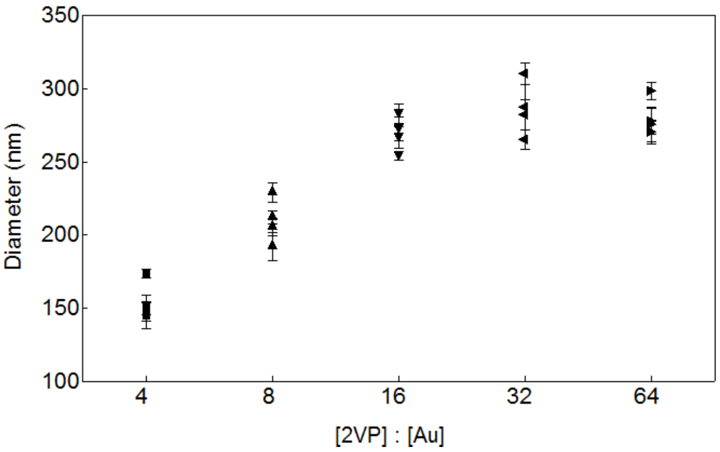

**Figure S2.** Diameter of the patterned block copolymer features (dwell time, 0.01 s) as a function of Au loading. The four points for each Au loading are from four different pens.

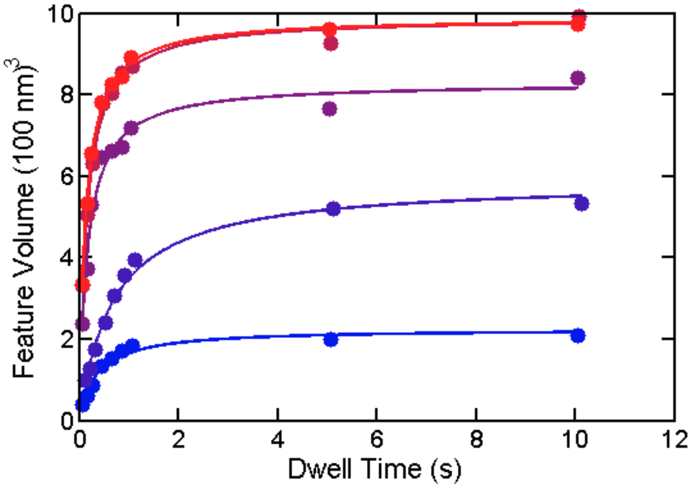

**Figure S3.** Fitting of polymer feature volume as a function of dwell time. Error bars are omitted for clarity.

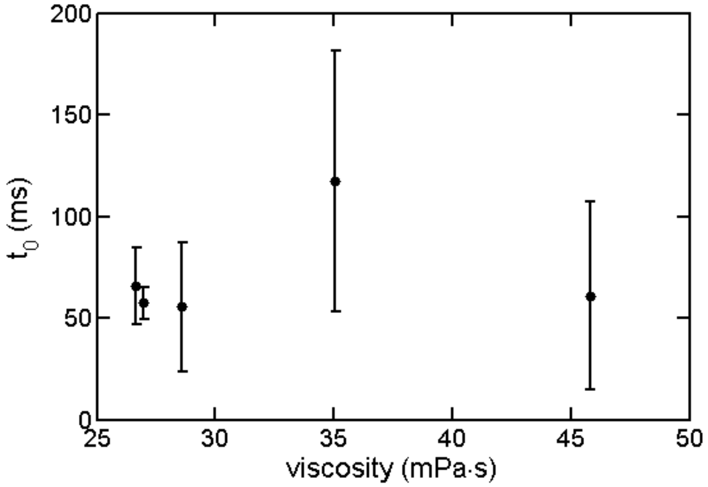

**Figure S4.** Offset time as a function of ink viscosity.

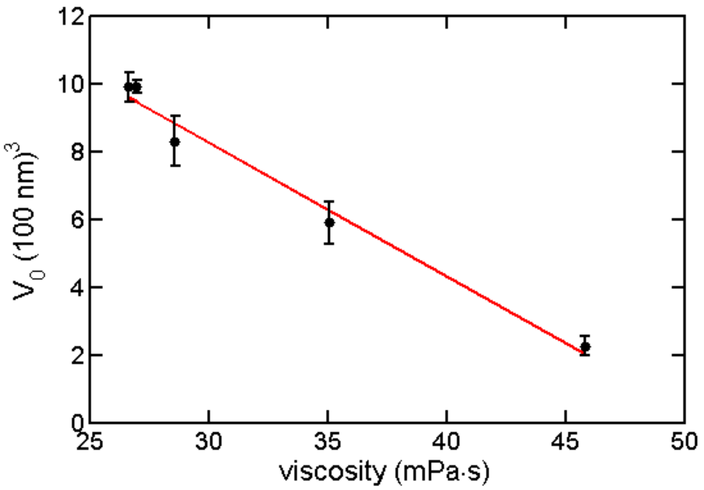

**Figure S5.** Maximum polymer volume as transferred *via* DPN as a function of ink viscosity.

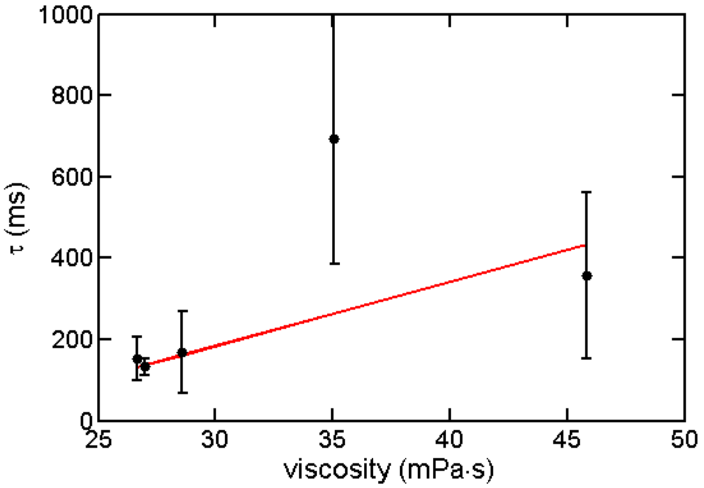

**Figure S6.** Saturation time as a function of ink viscosity.

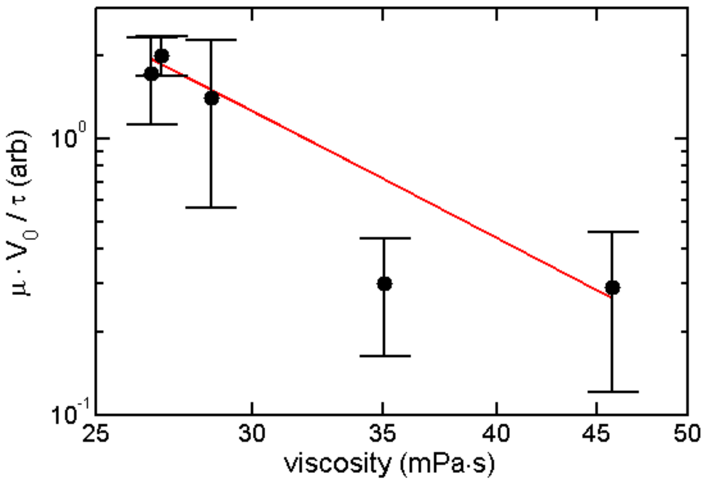

**Figure S7.** Initial driving force scaling as a function of ink viscosity.