

Solventless ordering of colloidal particles through application of patterned elastomeric stamps under pressure

Kahp Y. Suh^{a)}

School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, Korea

Hyunsik Yoon and Hong H. Lee

School of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

Ali Khademhosseini and Robert Langer

Division of Biological Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 9 February 2004; accepted 19 July 2004)

We report on an ordering phenomenon of polystyrene beads that occurs when pressure is applied to the colloidal particles between a solid substrate and a patterned elastomeric stamp while maintaining the temperature above the particle's glass transition temperature. The filling time is calculated using a simple two-dimensional squeeze flow theory, which successfully explains the effects of pressure, temperature, size of beads, and stamp geometries on the ordering time. © 2004 American Institute of Physics. [DOI: 10.1063/1.1795362]

Polymer colloids are interesting and versatile building blocks for the patterning of surfaces or fabrication of two-(2D) or three-dimensional (3D) microstructures.^{1–5} There are a number of approaches to forming well-ordered colloidal assemblies including the use of an external electric^{6–8} or intense optical field⁹ as well as the manipulation of the interaction potential^{10,11} in evaporating films. For these evaporating films, the assembly is governed by the attractive capillary immersion forces and convective particle flux caused by water evaporation (so called “convective assembly”).^{12,13} A more promising approach is colloidal epitaxy, in which the deposition of colloidal particles is carried out onto a lithographically modified or a microcontact printed substrate.^{14–16} In addition to these methods, microfluidic networks have been used to spontaneously pattern a suspension of latex particles.^{17–19} Similarly, latex particles have been patterned under pressurized flow by injecting through a narrow slit between two planar surfaces.^{20,21}

Here we report an ordering phenomenon that takes place when pressure is applied to the colloidal particles sandwiched between a solid substrate and a patterned elastomeric stamp while maintaining the temperature above the particle's glass transition temperature. Although the degree of ordering is not striking, it is intriguing that the particles can be assembled into the features of the stamp even in the dried state, i.e., without the aid of a solvent.

An illustration of the ordering process is shown in Fig. 1. The colloids used in this study consisted of monodisperse polystyrene (PS) microspheres (3.0, 1.1, or 0.46 μm in diameter, purchased from Aldrich) suspended in distilled water at various volume fractions (0.1%–10%). To obtain a relatively uniform distribution of particles on the substrate, the latex suspension was spin coated onto hydrophilic substrates such as glass or silicon dioxide at 1000–7000 rpm for 20 s (Model CB 15, Headway Research, Inc.). Hydrophobic surfaces could not be used since the suspension was washed away or dewetted immediately after spin coating. Depending

on the concentration and the coating speed, various fractional surface densities (n) were obtained ranging from 0.07 (± 0.02) to 0.93 (± 0.05). The samples were dried overnight at room temperature to ensure complete water evaporation. As the initial rough morphology does not allow for conformal contact between the stamp and the substrate, a flat metal object was loaded on top of the PDMS stamp to apply a pressure ranging from 1 to 10 N/cm^2 . Interestingly, even though the application of pressure during contact has been shown to lead to sagging or collapse of the unsupported areas,²² no such phenomenon was observed in our experiments, presumably due to the high aspect ratio of the PDMS stamp. To allow for the formation of colloidal patterns, the temperature was raised above the polymer's glass transition temperature (T_g) (>94 $^\circ\text{C}$ for PS beads) and annealed for a period of time ranging from 1 to 300 min. A glimmering color can be seen after the stamp removal, which is an indication of a successful ordering.

The ordered 2D or 3D microstructures were examined by optical microscopy (OM) and scanning electron microscopy (SEM) measurements (Fig. 2). As can be seen from Figs. 2(a)–2(d) (10 μm PDMS stamp and 3.0 μm PS beads, annealed for 25 min at 110 $^\circ\text{C}$ under a pressure of 10 N/cm^2), two distinct regions were observed: an ordered region that was patterned underneath the stamp and a ran-

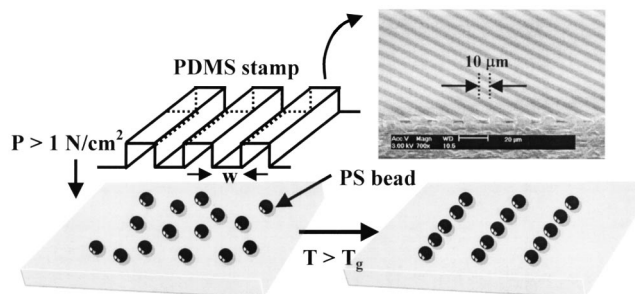


FIG. 1. Illustration of the experimental procedure. A cross-sectional SEM image is shown in the figure for the microstructure of a 10 μm PDMS stamp.

^{a)} Author to whom correspondence should be addressed; electronic mail: sky4u@snu.ac.kr

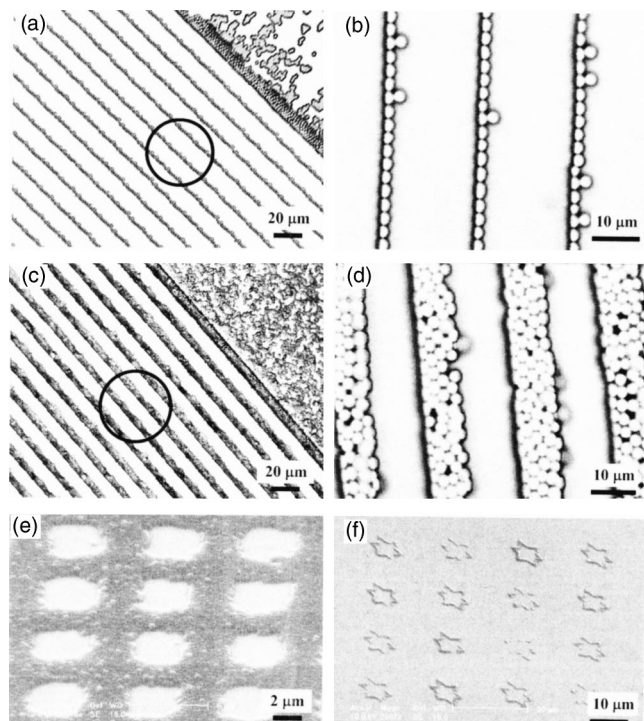


FIG. 2. Typical ordering results for various PS beads and PDMS stamps. (a)–(d) OM images of ordered $3.0\ \mu\text{m}$ PS beads along the channels of a $10\ \mu\text{m}$ PDMS stamp when annealed for 25 min at $110\ ^\circ\text{C}$ under a pressure of $10\ \text{N}/\text{cm}^2$. $n=0.31$ and 0.85 for (a) and (c), respectively. Magnified views [(b) and (d), circled regions] show a single or multiple lines of PS beads along the channel direction depending on the initial fractional density; (e) SEM image of an interconnected structure of PS beads for a PDMS stamp having $3\ \mu\text{m}$ cylinders (positive) and $0.46\ \mu\text{m}$ PS beads, annealed for 10 min at $120\ ^\circ\text{C}$ under a pressure of $10\ \text{N}/\text{cm}^2$; (f) SEM image of a star-shaped isolated structure. A PDMS stamp having $1\ \mu\text{m}$ voids (negative) and $0.46\ \mu\text{m}$ PS beads were used, annealed for 15 min at $110\ ^\circ\text{C}$ under a pressure of $10\ \text{N}/\text{cm}^2$.

domly distributed region outside the stamp. During the contact process, particles spontaneously migrated into the void space of the stamp and ordered along the line direction. For the ordering to take place, the step height of the stamp has to be higher than the bead size. Depending on the initial density of the particles, aggregated beads form single or multiple lines [Figs. 2(a) and 2(c)]. Since the temperature is higher than the glass transition temperature (T_g), PS beads continuously melt and merge with neighboring beads as time progresses, ultimately resulting in the fully connected or locally connected lines. Thus, one can tailor the shape and microstructure of the PS beads. As expected, the quality of the ordered structure is determined by the uniformity of the initial distribution of the beads. However, it is interesting that a monolayer of PS beads without many defects can be formed using this simple approach. In addition to ordered lines, an interconnected [Fig. 2(e)] or an isolated structure [Fig. 2(f)] can also be fabricated, providing various patterns that are not easily obtained by microfluidic channels.

We reported a process called capillary force lithography (CFL), in which a patterned PDMS stamp is placed onto a spin-coated polymer film and the temperature is raised above T_g to produce a negative replica of the stamp after the stamp is peeled off.^{23,24} Although the microbead patterning process described here may appear similar to CFL and the only difference is in the placement of polymer beads in place of a polymer film, the underlying mechanism is different. In CFL, capillarity and surface interactions are responsible for

the movement of the polymer, whereas it is unlikely that capillarity could play a role without the presence of a solution in the ordering process of PS beads. Instead, the physical pressure applied during the contact appears to be a more likely explanation for this behavior. If we envision that an elastic ball is confined between two soft plates with enough void space to accommodate the ball, it would be captured during the squeezing of both plates, provided that there are no special interactions between the ball and the plates. In a similar manner, when a viscoelastic body such as a PS bead is confined between an elastomeric stamp and a hard solid substrate, it may be possible that the particle spontaneously migrates into the void space of the stamp in response to the external pressure. One notable finding is that the migration is enhanced with an increase in temperature above T_g , which suggests that the mobility of PS beads below T_g is not sufficient to facilitate the assembly, or the PS beads are slightly pinned to the substrate such that a high temperature is needed to overcome the activation barrier of the movement. It is known that PS dewets easily on a PDMS surface.²⁵ Therefore, the migration of beads may have been aided by the high repulsion by the contact surfaces.

To gain an understanding on the ordering process, a 2D squeeze flow theory previously developed for imprint lithography is applied to estimate the time required to fill a cavity in the stamp with beads, t_r .^{26,27} The model allows for the calculation of the time required to displace a given amount of polymer of height h with a stamp of width, w . If we assume that the polymer melt is purely viscous, ideally adhered to the surfaces, incompressible and $w \gg h$, one can obtain

$$t_r = \frac{\eta w^2}{2p} \left(\frac{1}{h_f^2} - \frac{1}{h_0^2} \right), \quad (1)$$

where h_0 is the initial height of the polymer, h_f is the final height of the polymer, η is the polymer viscosity, and p is the normal pressure applied to the beads. If we further assume that h is an equivalent height when a bead is completely melted and flattened at the contact surface, $h_0 = \pi r^2 / (w/2)$ (r : bead radius). Since beads are initially isolated and the mass transfer is discrete (c.f. continuous mass transfer for polymer films), it is difficult to define h_f appropriately. The relation indicates that t_r becomes infinite as h_f goes to zero, which fails to explain the ordering process presented in this study. Thus, we redefine t_r as the time to reach half the initial thickness ($h_f = h_0/2$). Physically, this means that if a bead is squeezed with a 50% reduction in volume upon exposure to pressure, the ordering takes place and is completed instantaneously. With these assumptions, one can find

$$t_r = \frac{3\eta w^2}{2ph_0^2}. \quad (2)$$

From Eq. (2), it can be seen that the polymer viscosity should be decreased (by increasing temperature) and the applying pressure increased to reduce the ordering time, which is in agreement with our observations.

Although the above equation is based on some simplifications, the comparison between theory and experimental data is satisfactory, which is shown in Fig. 3. The relationship between zero shear viscosity (η_0) and temperature was determined using the William-Landel-Ferry (WLF) equation.²⁸

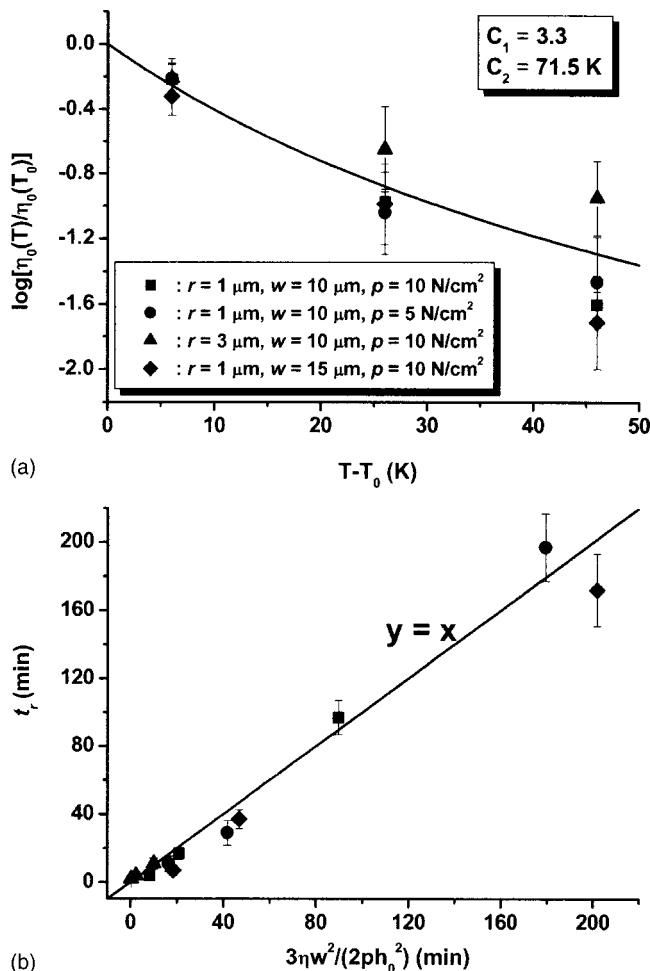


FIG. 3. (a) Calculation of zero shear viscosity (η_0) using the William-Landel-Ferry (WLF) equation, which gives $C_1=3.3$ and $C_2=71.5$ K for $\eta_0(T_0)=10^{12}$ Pa s; (b) comparison between theory ($y=x$) and experimental data at various conditions.

$$\log a_T = -\frac{C_1(T - T_0)}{C_2 + T - T_0} = \log \frac{\eta_0(T)}{\eta_0(T_0)} \quad (3)$$

The best fit to the experimental data was obtained with the following parameters: $T_0=367.15$ K, $C_1=3.3$, $C_2=71.5$ K where we used $\eta_0(T_0)=10^{12}$ Pa s since all polymers have a viscosity of roughly the same order of magnitude at their respective T_g 's.²⁸

A scattering of the data was observed, possibly due to the effects of wetting conditions and nonuniform pressure distribution during contact. It appears that all experimental errors have been incorporated into two fitting parameters, C_1 and C_2 , which may be different from other studies, considering the confined geometry presented in this work. It is interesting to note that the filling time sharply increases with decreasing size of the PS bead ($t_f \propto r^{-2}$). In fact, as mentioned earlier, it becomes nearly impossible to obtain uniform patterns when the size is less than a critical size, which should be a function of stamp geometry such as the aspect ratio [for example, $0.46 \mu\text{m}$ for $15 \mu\text{m}$ channels in Fig. 2(f)]. Physically, this sharp increase in the filling time can be explained as follows: (i) If the bead size decreases, the surface to volume ratio increases accordingly, resulting in a large contact area between the beads and the PDMS surface. This, in turn, would invalidate the assumption of ideal adhe-

sion at the surfaces in Eq. (1) and drastically increase the time required to fill the cavity. (ii) Smaller beads seem to merge quickly and be frozen at the contact surface, leading to incomplete migration of beads. Once the beads were melted and merged completely, it can be assumed that the mass transport within the void space and along the stamp follows the CFL process.

In summary, we have presented an ordering process of PS beads with a patterned PDMS stamp placed under pressure. This ordering is unique in that the particles migrate by means of physical pressure aided by elevated temperature, not through the action of convective assembly as in evaporating films.^{12,13} This approach could provide ways to study the movement of polymer beads under a confined geometry or, if necessary, to fabricate ordered 2D or 3D particle arrays when solvents need to be excluded during the ordering process.

This research was supported by a Grant (04K1401-01710) from Center for Nanoscale Mechatronics and Manufacturing, one of the 21st Century Frontier Research Programs, which are supported by the Ministry of Science and Technology, Korea.

¹B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1989).
²T. A. Witten, *Rev. Mod. Phys.* **71**, S367 (1999).
³S. Giasson, D. A. Weitz, and J. N. Israelachvili, *Colloid Polym. Sci.* **277**, 403 (1999).
⁴H. Y. Koo, D. K. Yi, S. J. Yoo, and D. Y. Kim, *Adv. Mater. (Weinheim, Ger.)* **16**, 274 (2004).
⁵J. M. Yao, X. Yan, G. Lu, K. Zhang, X. Chen, L. Jiang, and B. Yang, *Adv. Mater. (Weinheim, Ger.)* **16**, 81 (2004).
⁶M. Trau, D. A. Saville, and I. A. Aksay, *Science* **272**, 706 (1996).
⁷K. Q. Zhang and X. Y. Liu, *Nature (London)* **429**, 739 (2004).
⁸S. R. Yeh, M. Seul, and B. I. Shraiman, *Nature (London)* **386**, 57 (1997).
⁹S. L. Westcott, S. J. Oldenburg, T. R. Lee, and N. J. Halas, *Chem. Phys. Lett.* **300**, 651 (1999).
¹⁰C. A. Murray and D. H. van Winkle, *Phys. Rev. Lett.* **58**, 1200 (1987).
¹¹A. E. Larson and D. G. Grier, *Nature (London)* **385**, 230 (1997).
¹²N. D. Denkov, O. D. Velev, P. A. Kralchevsky, I. B. Ivanov, H. Yoshimura, and K. Nagayama, *Langmuir* **8**, 318 (1992).
¹³K. Nagayama, *Colloids Surf., A* **109**, 363 (1996).
¹⁴J. Aizenberg, P. V. Braun, and P. Wiltzius, *Phys. Rev. Lett.* **84**, 2997 (2000).
¹⁵B. F. Lyles, M. S. Terrot, P. T. Hammond, and A. P. Gast, *Langmuir* **20**, 3028 (2004).
¹⁶U. Jonas, A. del Campo, C. Krüger, G. Glasser, and D. Boos, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 5034 (2002).
¹⁷E. Kim, Y. Xia, and G. M. Whitesides, *J. Am. Chem. Soc.* **118**, 5722 (1996).
¹⁸G. A. Ozin and S. M. Yang, *Adv. Funct. Mater.* **11**, 95 (2001).
¹⁹D. G. Choi, H. K. Yu, S. G. Jang, and S. M. Yang, *Chem. Mater.* **15**, 4169 (2003).
²⁰S. H. Park, D. Qin, and Y. Xia, *Adv. Mater. (Weinheim, Ger.)* **10**, 1028 (1998).
²¹Y. N. Xia, Y. D. Yin, Y. Lu, and J. McLellan, *Adv. Funct. Mater.* **13**, 907 (2003).
²²A. Bietsch and B. Michel, *J. Appl. Phys.* **88**, 4310 (2000).
²³K. Y. Suh, Y. S. Kim, and H. H. Lee, *Adv. Mater. (Weinheim, Ger.)* **13**, 1386 (2001).
²⁴K. Y. Suh and H. H. Lee, *Adv. Funct. Mater.* **12**, 405 (2002).
²⁵G. Reiter, *Phys. Rev. Lett.* **87**, 186101 (2001).
²⁶L. J. Heyderman, H. Schift, C. David, J. Gobrecht, and T. Schweizer, *Microelectron. Eng.* **54**, 229 (2000).
²⁷R. B. Bird, R. C. Armstrong, and O. Hassager, *Fluid Mechanics, Dynamics of Polymeric Liquids* (John Wiley, New York, 1987).
²⁸J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley, New York, 1980).