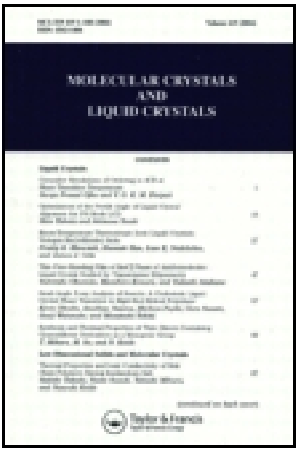

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Self-Assembled Monolayers Using Large-Size Polystyrene Particles

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Version of record first published: 16 May 2011

To cite this article: Miho Kawai, Kyohei Takano, Akira Nakajima, Toshihiro Isobe & Sachiko Matsushita (2011): Self-Assembled Monolayers Using Large-Size Polystyrene Particles, Molecular Crystals and Liquid Crystals, 539:1, 33/[373]-39/[379]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.566041

Mol. Cryst. Liq. Cryst., Vol. 539: pp. 33/[373]–39/[379], 2011
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.566041

Self-Assembled Monolayers Using Large-Size Polystyrene Particles

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Particle self-assembly was affected by various factors. A theoretical formula using particle concentration, water evaporation rates, and withdrawal rates of substrate during evaporation-driven self-assembly had already reported: However, it showed a lack of evidence for large-size particles (more than diameter 2,106 nm). Here, we suggest optimum fabrication conditions for large-size (3.0-μm dia.) particle monolayer on a horizontally-set glass substrate by the evaporation-driven self-assembly. Two parameters, the volumes of used suspension and the meniscus angles between the suspension and the substrate, were examined. The experimental formula was also constructed by developing the reported formula.

Keywords Artificial opal; colloidal crystal; particle array; polystyrene; self-organize

Introduction

A self-assembly technique is a simple and inexpensive preparation method [1,2]. The preparation of two-dimensional (2D) array, in which particles were periodically arrayed in layers, is one of the most significant techniques [3]. Various self-assembly techniques, developed; evaporation-driven self-assembly [4], electrophoretic deposition [5,6], spin-coating technique [7,8], etc., had been reported.

The patterning methods of the monolayers also reported such as the chemical treatment of particles and/or the substrate [9,10], or two different unlikely-mixed solutions [11,12]. The applications of the prepared monolayers were also reported such as a microlens [13], a diamond electron emitter [14] and a biosensor for detection of ligand cased Alzheimer's disease [15]. It can be said that the development of efficient fabrication of monolayers is very important in various fields of chemistry, physics, and medical science [16–18].

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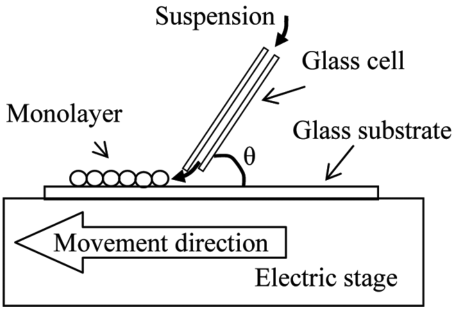

Figure 1. Schematic image of the evaporation-driven self-assembly to prepare a 2D array.

In the evaporation-driven self-assembly, a 2D array was fabricated by lifting up a substrate immersed in a particle suspension or by translating a substrate after formed a meniscus on the substrate [19–21]. The major factors of the evaporation-driven self-assembly are 1) the lateral capillary force in the meniscus formed between particles, and 2) the advective flow to the edge of meniscus. This evaporation-driven self-assembly enables us to fabricate mono-, di-, and multi-layers of particles in a relatively short preparation time.

The monolayer formation by evaporation-driven self-assembly had been achieved by controlling temperature and moisture, and the salt concentration of particle suspension [22,23]. Dimitrov, *et al.* had constructed a theoretical formula by introducing array densities, water evaporation rates, withdrawal rates of substrate, and convinced experimentally [24]. However, it seems not to be appropriate for large-size particles (more than diameter 2,106 nm). The preparation of wide monolayers of large-size particles would expand its applications especially in the biological field, e.g., single cell analysis, a filter for allergen particles (for example, 30 μm pollen dusts, several micrometers tick feces, and 3–6 μm pollens), and so on.

In this research, we suggest the optimum preparation conditions for monolayers, composed of large-size particles, fabricated horizontally on a glass substrate by the evaporation-driven self-assembly (Fig. 1). In the case of the horizontally set-up substrate, a glass cell in which the particle suspension was injected was required [21]. This glass cell enabled us to control two parameters, suspension volume and the glass cell angle θ [25–27]. The authors investigated to validate the efficient conditions for wide-area monolayer formation using large particles, concretely the efficient angle of glass cells and the suspension volume, and to construct an experimental formula based on the Dimitrov's theory [24].

Materials and Methods

Monolayers were formed with polystyrene spherical particles (PSt, Duke Scientific Co.; diameter 3.0 μm (CV < 5%), red fluorescent) using the developed devices by Matsushita, *et al.* The particles concentration was 1.0 wt%. The density was 1.05 g/ml. A small glass cell (Fig. 1) was used for preparation of the 2D arrays. This cell was composed of microscope cover glasses by handmade. The width of this cell was 23 mm; the gap width was 1 mm. A meniscus composed of the particle suspension could be formed between the glass cell and a nonfluorescent glass substrate (38 × 26 mm, thickness: 1.0–1.2 mm, Matsunami Co., Japan). The substrate was rinsed 3 times with distilled water and 99.8% methanol alternatively. The contact angle of the cleaned substrate surface was 16.9°. Detail procedure was reported in Ref. 21.

The slide glass was horizontally translated at a constant speed (4.0 μm/s) with the suspension meniscus. The suspension volume was 0.1 – 0.25 mL, and the glass cell angle was 35°–70°, respectively. The suspension was injected into a glass cell with a microsyringe. Layers formation was confirmed with optical microscopic observation (OLYMPUS, BX60, JAPAN). The maximum, minimum and average of the width of the monolayers thus formed were measured by a ruler with naked eyes. All experiments were carried out under room temperature 25.3°C (SD ± 2.7). The humidly was 44.4% (SD ± 8.3).

Results and Discussions

Monolayer Preparation

Under every experiment conditions, convective flow was occurred and striped particle arrays were formed. The particle flow was affected by the stick-slip motion as a source of friction at the suspension contact line [25]. Therefore, we evaluated the widths of the monolayers in front of the stick-slip patterns. Additionally, optical microscopy revealed that the particles were closely packed in layers (Fig. 2). The formation of monolayers, bi-layers and multilayers was confirmed at several experimental conditions.

The widths of the monolayers were showed in Figure 3, Table 1, and Figure 4. The maximum width of the monolayers was observed under two different conditions: the angle and the volume were 40° and 0.15 mL, or 55° and 0.2 mL, respectively. Monolayers could not be formed under the conditions over 45° using 0.25 mL suspension volume, resulting in no plot in Figure 3-d, because the 0.25 mL suspension was over flowed from the cell to the substrate because of

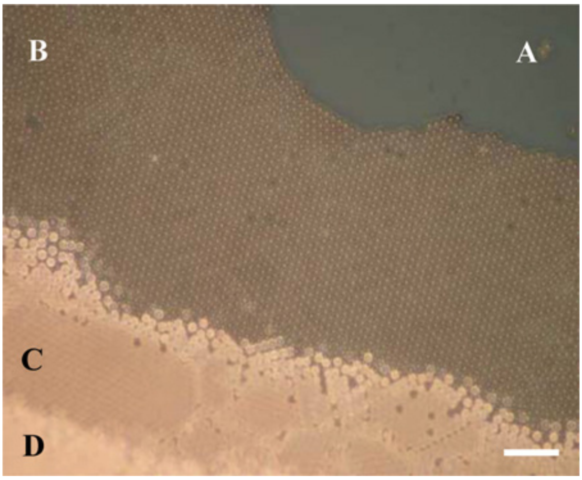

Figure 2. Optical microscopic image of the prepared 2D array. The glass substrate (A), monolayer (B), bilayer (C), and multilayer (D) were observed. The width of B was measured by a ruler with naked eyes. Scale bar indicates 100 μm.

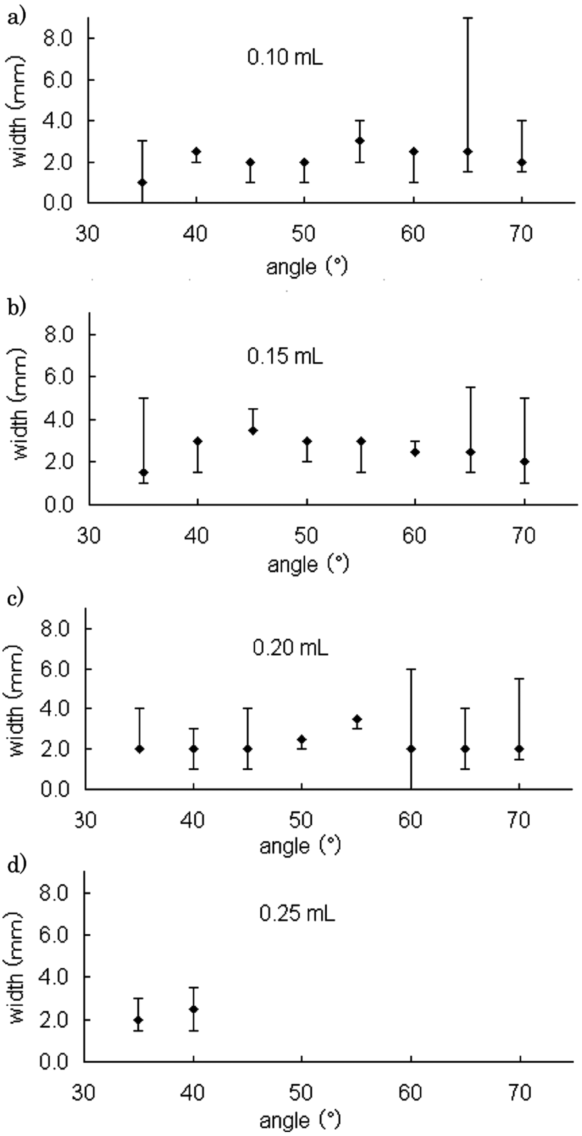

Figure 3. The monolayer width as glass cell's angles with particle suspension volumes: (a) 0.1 mL, (b) 0.15 mL, (c) 0.2 mL, and (d) 0.25 mL.

gravitational force. It was considered that the gravitational pressure of suspension against the slide glass at the outlet of the cell was one of the most significant factors to form monolayers (mentioned below). Those experimental results were revealed that the widths of the monolayers were depended on the glass cell angle and/or the suspension volume excepted temperature and humidly via evaporation-driven self-assembly. The monolayer widths thus formed were approximately from 1.0 to 3.5 mm. Here we should mention that the experimental values at lower angle (35°) or higher angles (over 65°) gave large error bars.

Table 1. Monolayer widths prepared by various experimental conditions. Asterisks (*) show the samples prepared under similar temperature and humidly

Volume (mL)	Angle θ (°)	Temperature (°C)	Humidly (%)	Monolayer width (mm)		
				Average	Minimum	Max
0.1	35	24.7	55.3	1.0	0.0	3.0
	40	25.6^{*1}	29.8	2.5	2.0	2.5
	45	24.0	38.5	2.0	1.0	2.0
	50	25.1	39.2	2.0	1.0	2.0
	55	25.0^{*2}	41.8	3.0	2.0	4.0
	60	26.3	34.5	2.5	1.0	2.5
	65	25.3^{*2}	41.7	2.5	1.5	9.0
	70	24.8	31.7	2.0	1.5	4.0
0.15	35	25.8	54.5	1.5	1.0	5.0
	40	27.8	39.6	3.0	1.5	3.0
	45	27.0	38.8	3.5	3.5	4.5
	50	26.3^{*4}	39.2	3.0	2.0	3.0
	55	26.1	38.3	3.0	1.5	3.0
	60	25.6	51.8	2.5	2.5	3.0
	65	24.8	59.8	2.5	1.5	5.5
	70	26.1	53.5	2.0	1.0	5.0
0.2	35	25.6	55.3	2.0	2.0	4.0
	40	26.8^{*4}	39.1	2.0	1.0	3.0
	45	25.8^{*3}	36.1	2.0	1.0	4.0
	50	26.0^{*3}	36.1	2.5	2.0	2.5
	55	24.4	42.5	3.5	3.0	3.5
	60	23.9	40.5	2.0	0.0	6.0
	65	23.5	48.2	2.0	1.0	4.0
	70	24.0^{*1}	38.5	2.0	1.5	5.5
0.25	35	25.6	55.8	2.0	1.5	3.0
	40	27.4	57.8	2.5	1.5	3.5

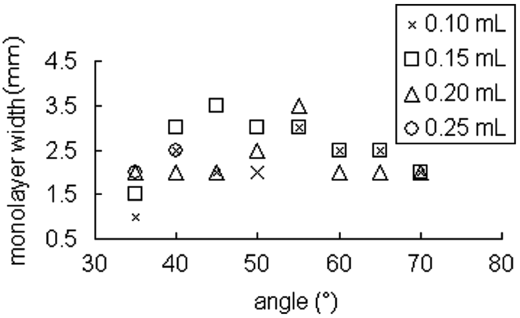

Figure 4. The angle- and suspension-volume dependence on the prepared monolayer widths.

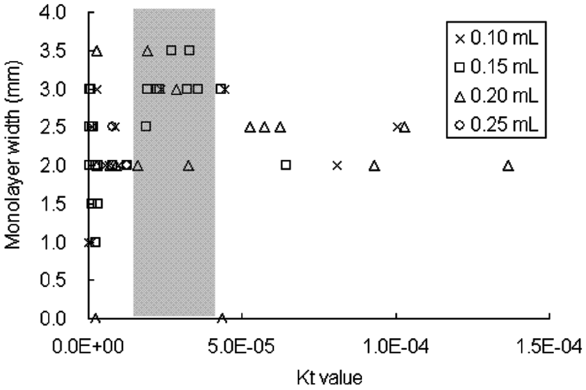

Figure 5. Relationship between K_t value and monolayer widths. Monolayer widths more than 3.0 mm were obtained when the coefficient K_t was $1.9 \times 10^{-6} \sim 3.3 \times 10^{-6}$.

The best results for the sake of the monolayer fabrication of the large-size particles (3.0 μm diameter) were obtained in 40°–55° and 0.15 mL, which bring a balance of the hydrostatic pressure.

Experimental Formula

Particle volume fraction in the suspension φ, water evaporation flux j_e [cm^2/s], and substrate moving velocity V_c [μm/s] was conducted as factors for theoretical formula of layer's fabrication [24]. The formula signified that monolayer widths should be constant. However, the widths of our formed monolayers were varied with the suspension volume and the cell's angle in our experiments. Here we attempt to reconstruct a new experimental constant K_t such as,

$$K_t = \frac{(\mathrm{mg} \cdot \cos\theta)^3 \left(T/M^2\right)^4 \beta j_e \phi}{V_c^3 (1 - \phi)}$$

Five parameters, "temperature; T [K]", "moisture; M [%]", "glass cell's angle; θ [radian]", "suspension volume; m [g]" and "gravity acceleration; g [9.8×10^{-2} cm/s^2]" were added in the original Dimitrov's formula. Former 2 parameters, T and M, represent the change of the water evaporation speed by temperature and moisture, which was originally included in j_e. The latter 3 parameters represent the gravity effect.

We attempted the compatibility verification between the constructed experimental constant and our experimental results. Consequently, when K_t values were $1.9 \times 10^{-6} \sim 3.3 \times 10^{-6}$, monolayer more than 3.0 mm width could be fabricated (Fig. 5). The authors should point out that the monolayer widths fabricated by more than 0.20 mL suspension volume were not corresponded with our experimental constants (Fig. 5). We consider that the hydrostatic pressure of the particle suspension on the substrate is the factor of poor reproducibility as well as the gravitational effect.

Conclusions

We tried to prepare self-assembled monolayers using large-size polystyrene particles (3.0 μm diameter) in a wide area by varying of the glass cell angle and suspension volume. The cell angle of 45°–55° and the suspension volume of 0.15 mL were well-balanced conditions and could prepare monolayers in wide area. An experimental constant was also constructed for efficient preparation of wide-area monolayers on horizontally substrate. Generally, monolayers fabrication of large-size particle by self-assembly has been difficult because of the gravitational force. Here, we suggest an experimental constant about evaporation-driven self-assembly by controlling the glass cell's angle.

Acknowledgment

The authors thank to Dr. Erito Kazawa in Tokyo Metropolitan Industrial Technology Research Institute, and Mr. Yohey Shibuya in College of Humanities and Sciences, Nihon University. This work is partially supported by Grant-in-aid for young scientists, Japan society for the promotion of the science (21750024), and Nihon University Strategic Projects for Academic Research.

References

[1] Prevo, B. G., & Velev, O. D. (2004). *Langmuir*, *20*, 2099–2107.
[2] Dushkin, C., Miwa, T., & Nagayama, K. (1998). *Chemical Physics Latters*, *285*, 259–265.
[3] Denkov, N. D., Velev, O. D., Kralchevsky, P. A., Ivanov, I. B., Yoshimura, H., & Nagayama, K. (1993). *Nature*, *361*, 26.
[4] Kumnorkaew, P., Ee, Y.-K., Tansu, N., & Gilchrist, J. F. (2008). *Langmuir*, *24*, 12150–12157.
[5] Giersig, M., & Mulvaney, P. (1993). *Langmuir*, *9*, 3408–3413.
[6] Trau, M., Saville, D. A., & Aksay, I. A. (1996). *Science*, *272*, 706–709.
[7] Döllefeld, H., Weller, H., & Eychmüller, A. (2001). *J. Phys. Chem. B*, *106*, 5604–5608.
[8] Chushkin, Y., Ulmeanu, M., Luby, S., Majkova, E., Kostic, I., Klang, P., Holy, V., Bochnicek, Z., Giersig, M., Hilgendorff, M., & Metzger, T. H. (2003). *J. Appl. Phys.*, *94*, 7743–7748.
[9] Himmelhaus, M., & Takei, H. (2002). *Phys. Chem. Chem. Phys.*, *4*, 496–506.
[10] Masuda, Y., & Koumoto, K. (2004). *Journal of Dispersion Science and Technology*, *25*(4), 503–511.
[11] Hayward, R. C., & Saville, D. A. (2000). *Nature*, *404*(6733), 56–59.
[12] Tanaka, M., Shimamoto, N., Tanii, T., Ohdomari, I., & Nishide, H. (2006). *Science and Technology of Adv. Mat.*, *7*, 451–455.
[13] Hayashi, S., Kumamoto, Y., Suzuki, T., & Hirai, T. (1991). *J. Colloid Interface Sci.*, *144*, 538–547.
[14] Okuyama, S., Matsushita, S. I., & Fujishima, A. (2000). *Chem. Lett.*, 534–535.
[15] Haes, A. J. (2005). *J. Am. Chem. Soc.*, *127*, 2264–2271.
[16] Langer, G. (2006). *Appl. Phys. Lett.*, *89*, 261104.
[17] Himmelhaus, M. (2000). *Sensors and Actuators B*, *63*, 24–30.
[18] Im, S. H. (2002). *Appl. Phys. Lett.*, *80*(22), 4133–4135.
[19] Dimitrov, A. S., & Nagayama, K. (1995). *Chem. Phys. Lett.*, *243*, 1995.
[20] Gu, Z. Z., Fujishima, A., & Sato, O. (2002). *Chem. Mater*, *14*, 760–765.
[21] Matsushita, S., Miwa, T., & Fujishima, A. (1997). *Langmuir*, *13*, 2582–2584.
[22] Rakers, S. (1997). *Langmuir*, *13*, 7121–7124.
[23] Rodner, S. C. (2002). *Langmuir*, *18*, 9327–9333.
[24] Dimitrov, A. S., & Nagayama, K. (1996). *Langmuir*, *12*, 1303–1311.
[25] Matsushita, S. I., & Shimomura, M. (2003). *Mol. Cryst. Liq. Cryst.*, *406*, 111/[305]–118/[312].
[26] Ohzono, T., Matsushita, S. I., & Shimomura, M. (2005). *Soft Matter*, *1*, 227–230.
[27] Matsushita, S. I., & Shimomura, M. (2006). *Colloids and Surfaces A*, *284–285*, 315–310.