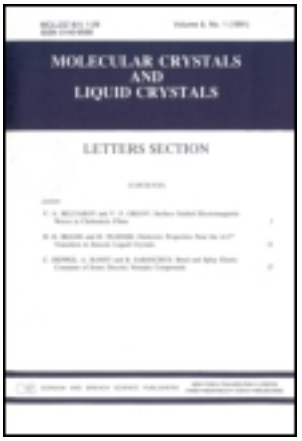

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Study on Micron-Sized Colloidal Ink Formulations and Colloidal Patterns by Inkjet Printing

Younghwan Kwon [a]
[a] Department of Chemical Engineering , Daegu University , Gyeongsan , Gyeongbuk , 712-714 , Korea
Published online: 16 Dec 2013.

To cite this article: Younghwan Kwon (2013) Study on Micron-Sized Colloidal Ink Formulations and Colloidal Patterns by Inkjet Printing, Molecular Crystals and Liquid Crystals, 584:1, 123-130, DOI: 10.1080/15421406.2013.849474

To link to this article: http://dx.doi.org/10.1080/15421406.2013.849474

Mol. Cryst. Liq. Cryst., Vol. 584: pp. 123–130, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.849474

Taylor & Francis
Taylor & Francis Group

Study on Micron-Sized Colloidal Ink Formulations and Colloidal Patterns by Inkjet Printing

YOUNGHWAN KWON*

Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk 712-714, Korea

The feasibility of inkjet printing of colloidal dispersion inks to arrange colloids in desired locations was investigated with different ink formulations and inkjet process variables. In order to maintain the structural stability of colloidal patterns fabricated on the substrate from externally applied forces such as mechanical, chemical and thermal stimuli, thermally curable binder was formulated into the colloidal ink formulations. Circularly aggregated colloidal pattern uniformly covered with the binder coating was created using a piezoelectric inkjet on a polymer substrate, indicating that colloidal micro-patterning by inkjet printing could be an effective method to control geometry of colloidal patterning on substrates.

Keywords Binder; colloidal pattern; colloidal particle; ink formulation; inkjet printing; surface tension

Introduction

Geometrical patterning in desired locations has become an increasingly important tool because of its broad range of applications, particularly for various biomedical applications and electrical devices such as light emitting diodes and film transistors. For generating desired patterns, many lithographical techniques have been extensively studied such as photolithography, dip-pen nanolithography, scanning probe lithography, and microcontact printing. In contrast to these lithographical techniques, inkjet printing has many attractive advantages as a fabrication method of micro-patterned structures such as simplicity, arbitrary geometries, low cost of process, low usage of materials, and flexibility [1–4]. Since the inkjet printing ejects the ink in a chamber through a fine nozzle by a thermal bubble or piezoelectric actuator, the inkjet printing process works by separately ejecting small amount of ink droplets with typically 1∼20 pL by the actuator [5,6].

We report the feasibility of piezoelectric inkjet printing of colloidal dispersion inks for geometrical patterning to arrange colloids in desired locations. However, for high resolution printing, inkjet printing system requires fine nozzles with very small diameter because the droplet size of ink is about two times larger than the nozzle diameter. Therefore, it is not simple to create well-defined colloid micro-patterns by piezoelectric inkjet printing system,

*Address correspondence to Younghwan Kwon, Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk 712-714, Korea, Tel.: +82-53-850-6561; Fax: +82-53-850-6569. E-mail: y_kwon@daegu.ac.kr

Table 1. Summary on physical properties of solvents used in ink formulations

Solvents	Contact angle (°)	Surface tension @20 °C (mN/m)	Boiling point @760 mmHg (°C)	Viscosity @25 °C (cP)
GBL	48.9	40.4	204∼206	1.7
EGPE	49.0	42.0	244	21.5
PGPE	45.2	38.1	243	25.2

since inkjet printing of heterogeneous colloidal particles frequently causes serious problems such as nozzle clogging, bubbles, precipitation, and uncontrollable drying patterns. In addition, maintaining the structural stability of colloidal patterns fabricated on the substrate from externally applied forces such as mechanical, chemical and thermal stimuli is still challenge for successful inkjet printing of colloidal ink.

In this study, polystyrene (PS) colloid (diameter = 3 μm) inks were formulated with thermally curable acrylic binder in organic solvents. The acryl binder was used to immobilize the PS colloidal particles on the substrate by covering them with thermally and chemically robust film. The thermal stability and chemical resistance of thermally cured acryl binder were investigated. Inkjet printing was conducted on a plastic substrate by using a piezoelectric inkjet printer with 20 μm of an internal nozzle diameter and about 20 pL of drop volume. The inkjet printability of colloidal inks was systematically investigated with different ink formulations and inkjet process variables.

Experimental

Materials

Reagent grades of solvents such as ethylene glycol phenyl ether (EGPE), propylene glycol phenyl ether (PGPE), *N*-methy pyrrolidone (NMP) and γ-butyrolactone (GBL) were purchased from Sigma-Aldrich Co. and used without further purification. Polystyrene colloids (Polybead® Microspheres, Dry from, with dia. = 3.00 μm) with surface hydroxyl groups were obtained from Polysciences, Inc.

Table 2. Summary on ink formulations and their properties

Binder Content	Solvent mixture (w/w)		Viscosity @25 °C	Contact angle	Diameter of 1
(wt%)	EGPE	GBL	(cP)	(°)	drop of ink (μm)
0.1	8	2	7.9	40.0	10–12
0.5	8	2	8.3	39.5	10–12
1.5	7	3	8.2	40.5	13–14
2.5	6	4	6.8	39.6	18–19
5.0	5	5	7.4	40.0	22–23
10.0	3	7	9.8	40.5	28–39

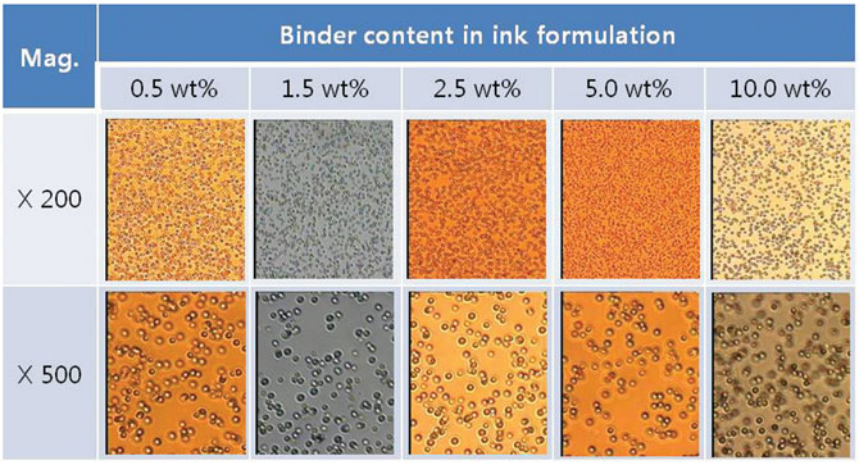

Figure 1. Optical images of PS colloidal ink formulations with different percentage of binder.

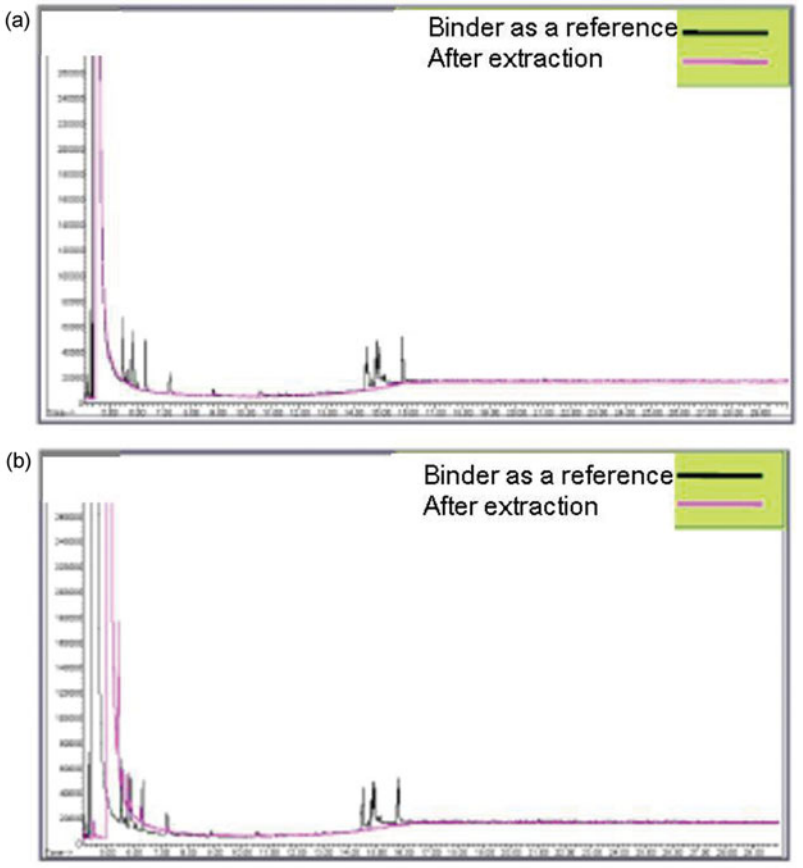

Figure 2. GC-Mass spectroscopic results of the cured binder coating extracted with (a) GBL and (b) NMP.

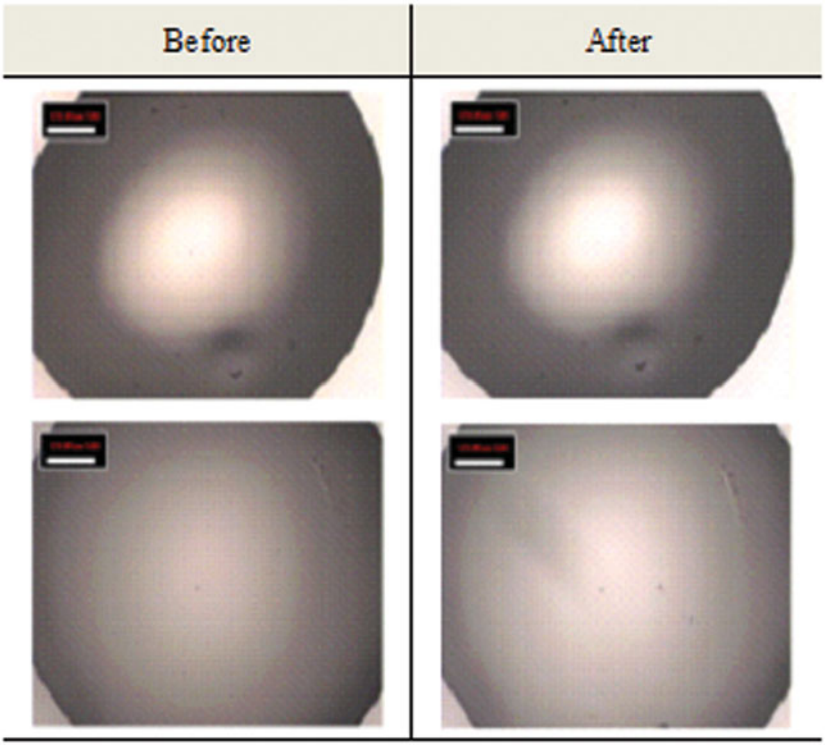

Figure 3. Photographs of the cured binder coatings before and after thermal treatment at 230 °C for 30 min.

Preparation of PS Colloidal Inks

The PS colloidal inks used in this experiment were prepared as follows. First, PS colloid solution was prepared by weighing 1 wt% of PS colloids in organic solvent mixtures (GBL/EGPE or GBL/PGPE) and ultrasonically dispersed for 1 h. Then, predetermined amount of thermally curable acryl binder (100 KOH mg/g of acid value, 450 eq of acryl equivalent, and 48 wt% of solid content in dipropylene glycol methyl ether) was added and stirred for 1 h, which resulted in the PS colloidal ink for inkjet printing.

Characterization

Contact angle measurement was performed to measure contact angle of solvents and ink formulations using DSA100MS (KRUSS GmbH). The dispersion of PS particles in ink formulations was monitored using optical microscope (MHL-150, Olympus Corp.). The viscosity of solvents and ink formulations was measured using rheometer (RE105L, Toki Sangyo Co., Ltd.). The experiment was performed using 1 mL of sample under 10 rpm for 180 sec at 25 °C. The adhesion of thermally cured acryl binder on the substrate was evaluated by the cross-cut peeling test according to ASTM D-3359. GC-Mass spectroscopy (GCMS-QP2010 Plus, Shimadzu Co.) was used to measure chemical stability of thermally cured acryl binder. The extract of the cured binder from different organic solvents such as NMP and GBL was analyzed and the result was compared with uncured binder as

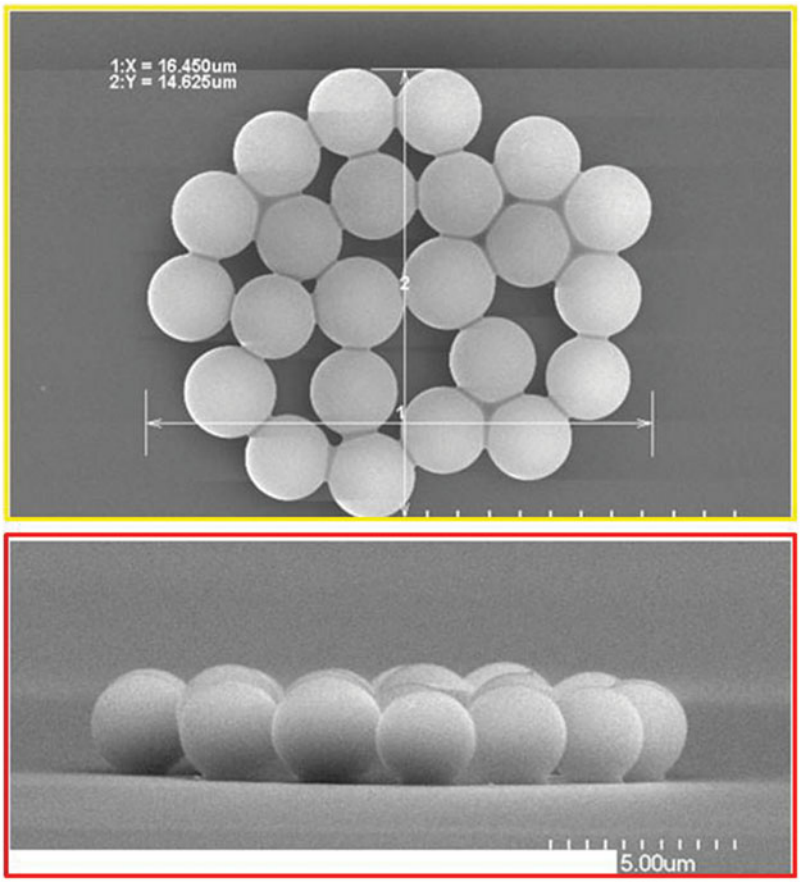

Figure 4. FE-SEM images of PS colloidal pattern fabricated using an ink formulation containing 0.1 wt% of the binder after inkjet printing and drying/curing process.

a reference. The morphology of PS colloid patterns was examined using field emission scanning electron microscopy (FE-SEM, S-4300, Hitachi) at a voltage of 15 kV.

Results and Discussion

The selection of solvent is the key step for colloidal ink formulations. A small amount of polymer and micron-sized colloidal particles in ink significantly can change rheological properties of the ink, and thereby the inkjet printability can be strongly affected [7–12]. Table 1 shows the contact angle, surface tension, boiling point and viscosity of solvents used in ink formulations. First of all, the homogeneity of colloidal ink is a prerequisite because poor solvents lead to polymer precipitation and colloidal agglomeration, eventually clogging the nozzle. All the solvents shown in Table 1 provided homogeneous solution with uniformly dispersed PS colloidal particles.

Optimum range of viscosity of ink has been reported to be below 10 cP in piezoelectric inkjet printing [13–15]. The force generated by a piezoelectric inkjet printer may be unable to eject ink drops through inkjet nozzles at higher viscosity [8,9,13]. However, too lower viscosity may also cause undesired satellite drops on a substrate. Boiling temperature of

solvents influences on the evaporation rate of solvents in ink droplets ejected. Generally, solvents with lower boiling point have incredibly short evaporation time, resulting in frequent nozzle clogging as well as uncontrollable drying patterns of ink droplets on the substrate. Considering the viscosity and boiling point of solvents, mixed GBL/EGPE (or PGPE) solvent system is anticipated for PS colloidal ink formulations.

Surface tension allows spherical droplets to emerge from inkjet nozzles, and contact angle of ink droplets on a substrate affects the pattern accuracy and resolution. The surface tension of inks for piezoelectric inkjet printing should be in the range of 30–70 mN/m, enough to prevent dripping of the ink from the nozzle [14–16]. The contact angle of ink droplets on the substrate should be higher than 40°, enough to allow high resolution of patterns formed after inkjet printing. The surface tensions and contact angles of all the solvents in Table 1 were also within the range as described previously.

Table 2 summarizes properties of PS colloidal ink formulations for inkjet printing. For the inkjet printing, the viscosity of ink formulations was required to be lower than 10 cP at 25 °C. The viscosity of the PS colloidal ink was found to be mostly determined by the weight percentage of binder, exhibiting that the viscosity of the ink increased with the binder content in the ink formulations. By adjusting the ratio of GBL/EGPE solvent mixtures, therefore, the viscosity of all the ink formulations containing the binder contents from 0.1 wt% to 10 wt% was kept to be similar range of around 10 cP, which was an acceptable range of viscosity for inkjet printing. The contact angles of ink formulations on the substrate were constant around 40° due to similar polarity of two solvents used, and were not influenced by weight percentage of the binders added in ink formulations. However, drop size of ink formulations after inkjet printing and drying/cure process increased with increasing the percentage of the binder in ink formulations. The dispersion of PS colloidal particles in ink formulations was measured by optical microscope. Figure 1 presents optical photographs of ink formulations which are the same compositions shown in Table 2. These results indicated that PS colloidal particles were not aggregated but well dispersed in ink formulations.

The binder in ink formulations was used to immobilize the PS colloidal particles on the substrate by covering them with thermally and chemically robust coating. Thermally curable binder solution was cast on a glass substrate and cured in a convection oven at 210 °C for 30 min. for investigating chemical, thermal and adhesive properties of cured binder coating itself. In case of chemical stability test, the binder film cured on the glass substrate was immersed in NMP and GBL, respectively, at room temperature for 1 h. Each organic solvent collected from the experiment was analyzed using GC-Mass spectroscopy, as presented in Fig. 2. Compared with those of uncured binder as a reference, GC-Mass data did not show any trace of extracts from the binder coating, indicating the formation of chemically resistant coating.

The binder film cured on the glass substrate was vertically positioned in a convection oven and thermally treated at 230 °C for 30 min to test the thermal stability. Figure 3 shows photographs of the cured binder film before and after thermal treatment. Under the experimental condition employed in this study, the shape and appearance of cured film were not changed, being supportive of the formation of thermally stable coating. In addition, adhesion of the binder coating was evaluated by 10 × 10 cross-cut peeling test. Evaluation was carried out on the binder coating film cured on the glass substrate, and measured to be 100/100, showing that no peeling was observed in the interface between the cured binder coating and the glass substrate.

We were able to carry out inkjet printing of PS colloidal inks on a substrate, after the inkjet printability of PS colloidal inks was systematically investigated, shown in Table 2,

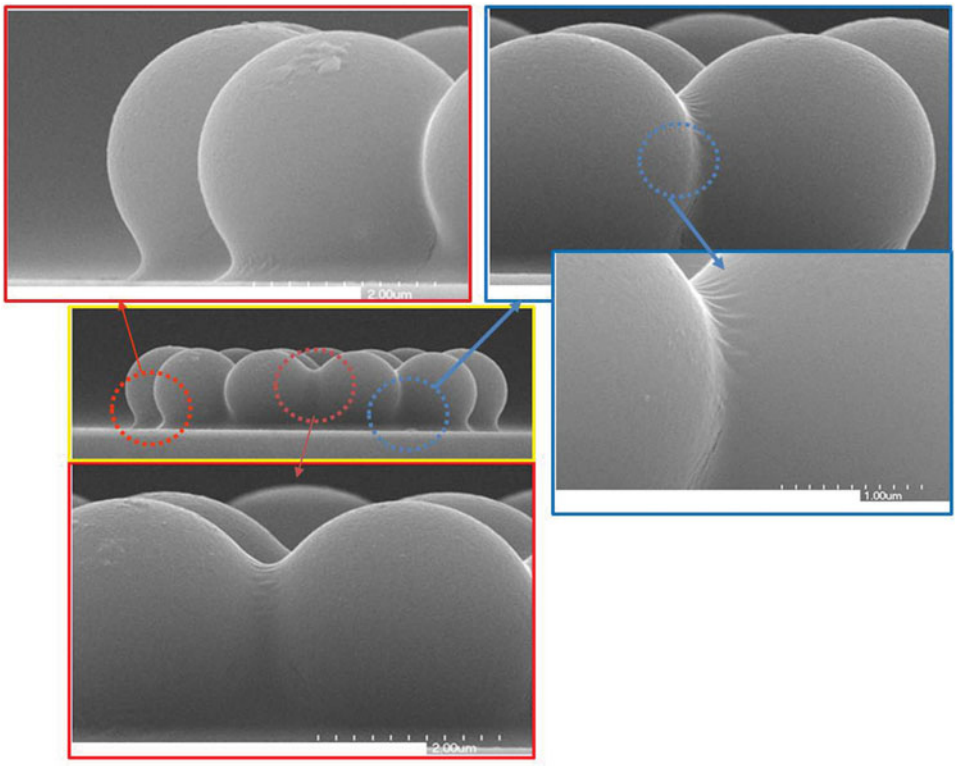

Figure 5. FE-SEM images of PS colloidal pattern fabricated using an ink formulation containing 5 wt% of the binder after inkjet printing and drying/curing process.

under different inkjet process variables. We specifically observed the morphology of PS colloidal particles formed after ejecting 1 drop of PS colloidal inks containing various percentage of the binder, followed by evaporating the mixed solvents in the ink and curing the remaining binder at 190 °C for 20 min. Figure 4 shows FE-SEM image of PS colloids after ejecting 1 drop of PS colloidal ink formulated with 0.1 wt% of the binder, and indicates a circular shape of PS colloidal aggregation with diameter size in the range of 14∼16 μm. This result implied that PS colloidal particles in the ink droplet were gathered into the center of the ink droplet during the evaporation of ejected ink droplet on the substrate. This might be originated from higher contact angle of the ink droplet ejected on the substrate with the evaporation time, because of the use of solvents with high surface tension in ink formulations. After curing process, therefore, the aggregated PS colloidal particles were nicely constrained in a circular pattern shape, and covered with very thin film of the cured binder, especially in interfaces between the contacted PS colloidal particles.

The effect of the content of binder in ink formulations was studied in detail. Figure 5 presents FE-SEM images of PS colloids after ejecting 1 drop of PS colloidal ink formulated with 5.0 wt% of the binder. As the content of the binder in ink formulations increased, the uniformly coated film of the cured binder was readily recognized over the aggregated PS colloids. These overall results showed the feasibility of inkjet printing of PS colloidal inks and fabrication of circularly aggregated PS colloids uniformly covered with mechanically robust, thermally stable and chemically resistant coating.

Conclusions

We have fabricated micron-sized PS colloidal ink formulations and shown the feasibility of the piezoelectric inkjet printing of these colloidal dispersion inks for geometrical patterning to arrange colloids in desired locations. As a result, circular pattern of colloidal particles was created on the substrate and uniformly covered with thin film of the cured binder. The uniform thin film coating could be expected to immobilize the structural integrity of colloidal patterns from mechanical force as well as to protect it from externally applied thermal and chemical stimuli.

Acknowledgment

This work was in part supported by Daegu University Research Grant 2013.

References

[1] Yu, J. H., Kim, S. Y., & Hwang, J. (2007). *Appl. Phys. A*, *89*, 157.
[2] Kim, J., Oh, H., & Kim, S. S. (2008). *Aerosol Sci.*, *39*, 819.
[3] (a) Wang, K., Paine, M. D., & Stark, J. P. W. (2009). *J. Mater. Sci.: Mater. Electron.*, *20*, 1154. (b) Wang, K., Paine, M. D., & Stark, J. P. W. (2009). *J. Appl. Phys.*, *106*, 024907.
[4] (a) Wang, X., Carr, W. W., Bucknall, D. G., & Morris, J. F. (2012). *Int. J. Multiphase Flow*, *38*, 17. (b) Sowade, E., Hammerschmidt, J., Blaudeck, T., & Baumann, R. R. (2012). *Adv. Eng. Mat.*, *14*, 98.
[5] Cho, M. S., Choi, W. H., Kim, S. G., Kim, I. H., & Lee, Y. (2010). *J. Nanosci. Nanotechnol.*, *10*, 6888.
[6] Lee, K.-J., Kim, N., Hong, S.-J., Lee, K. B., Lee, D.-J., Oh, J. H., Byun, Y., & Choa, Y.-H. (2010). *J. Nanosci. Nanotechnol.*, *10*, 3350.
[7] de Gans, B.-J., Kazancioglu, E., Meyer, W., & Schubert, U. S. (2004). *Macromol. Rapid Commun.*, *25*, 292.
[8] Cooper-White, J. J., Fagan, J. E., Tirtaatmadja, V., Lester, D. R., & Boger, D. V. (2002). *J. Non-Newtonian Fluid Mech.*, *106*, 29.
[9] Christanti, Y., & Walker, L. M. (2001). *J. Non-Newtonian Fluid Mech.*, *100*, 9.
[10] Shore, H. J., & Harrison, G. M. (2005). *Phys. Fluids.*, *17*, 033104.
[11] Christanti, Y., & Walker, L. M. (2002). *J. Rheol.*, *46*, 733.
[12] Mun, R. P., Byars, J. A., & Boger, D. V. (1998). *J. Non-Newtonian Fluid Mech.*, *74*, 285.
[13] de Gans, B.-J., Duineveld, P. C., & Schubert, U. S. (2004). *Adv. Mater.*, *16*, 203.
[14] de Gans, B.-J., & Schubert, U. S. (2003). *Macromol. Rapid Commun.*, *24*, 659.
[15] Yun, Y. H., Kim, J. D., Lee, B. K., & Cho, Y. W. (2009). *Macromol. Res.*, *17*, 197.
[16] Ngamna, O., Morrin, A., Kilard, A. J., Moulton, S. E., Smyth, M. R., & Wallace, G. G. (2007). *Langmuir.*, *23*, 8569.