

# Self-Assembled Poly(styrene-*co*-*N*-isopropylacrylamide) Film Induced by Capillary Force

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**ABSTRACT:** The monodisperse poly(styrene-*co*-*N*-isopropylacrylamide) (poly(St-*co*-NIPAAm)) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation were induced by capillary forces to self-assemble, and formed the two-dimensional films on the clean glassware wafer substrates. The morphologies of the two-dimensional films were characterized by scanning electron microscopy (SEM) and atom force microscopy (AFM). The results showed that monodisperse poly(St-*co*-NIPAAm) particles

could form ordered two-dimensional films by capillary forces. With NIPAAm concentration increasing, there gradually appeared surface undulations or surface defective region on the two-dimensional films. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 3514–3519, 2006

**Key words:** colloids; films; self-assembly; atomic force microscopy

## INTRODUCTION

Self-assembly is an important and pervasive characteristic of colloid<sup>1,2</sup> as well as biological systems, the colloidal particles can be prepared from well-defined 2D or 3D spatial configurations by self-assembly technologies. These formed well-defined configurations can display unique optical, electrical, and mechanical properties.<sup>3–5</sup>

Alfrey et al.<sup>6</sup> first reported that colloidal particles self-assembled into dry films with a highly ordered structure or macrocrystals, which displayed unique optical properties such as Bragg diffraction of light, and thus iridescence. Then, different spatial configurations including 2D films and 3D colloid crystals, which were prepared by the different self-assembly methods including spin-coating,<sup>7</sup> patterned templates,<sup>8</sup> electrophoretic deposition,<sup>9</sup> were studied. It was well known that capillary forces were the interactions between particles mediated by fluid interfaces. Recently, the interest in capillary forces has grown because of their recognizable importance for the self-assembly of colloid particles.<sup>10</sup> Cong and Cao<sup>11</sup> reported that colloidal crystallization was induced by capillary forces, and the two packing modes (hexagonal and face centered cubic) of the colloidal crystals are formed by deposition of the particles on an inclined substrate. The effects of temperature and surfactant on the array fashions of the particles as well as

the packing modes of the crystal have also been investigated. Yin et al.<sup>12</sup> reported a general approach that used geometrical confinement and attractive capillary forces to self-assemble two different types of monodisperse spherical colloids into a specific class of nonspherical colloids: asymmetric dimers. Chung et al.<sup>13</sup> reported that poly(St-*co*-MAA) microspheres could self-assemble to prepare the high-quality colloidal crystals through a novel capillary-enhanced process. This new self-assembly technique enhanced the capillary effect by controlling the humidity to result in the effective operation of the primary and secondary capillary forces during evaporation. Using this method, the high-quality colloidal crystal could be fabricated on a large area in a relatively short time.

As we all know that microwave irradiation was a special heating energy, and it had the significant advantages over the conventional thermal methods. Many researchers reported that stable colloid particles were prepared by emulsifier-free emulsion polymerization with microwave irradiation, and the size distributions of the obtained colloid particles with microwave irradiation were narrower than those prepared by conventional heating method.<sup>14,15</sup> In this study, we prepared the monodisperse poly(St-*co*-NIPAAm) particles by emulsifier-free emulsion polymerization with microwave irradiation, and the obtained monodisperse poly(St-*co*-NIPAAm) particles were induced by the capillary forces to self-assemble, and formed the two-dimensional films on the clean glassware wafer substrate. The morphologies of the two-dimensional films were mostly studied.

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## EXPERIMENTAL

### Materials and apparatus

Styrene (St) was distilled to remove the inhibitors in vacuum and stored at 4°C until use. *N*-isopropylacrylamide (NIPAAm) was of reagent grade and obtained commercially from Sigma–Aldrich, which was purified by recrystallization from a mixture of toluene–hexane (v/v: 1/1). The water was deionized before use. Potassium persulfate (KPS) was purified by recrystallization in the deionized water. The commercial microwave oven was modified so as to use. And the microwave frequency was 2450 MHz; the output power was all continuously adjustable within the range of 65–650 W.

### Preparation of poly(St-co-NIPAAm) particles

Water (90.0 mL) was introduced into a 250 mL three-neck, round-bottom flask equipped with a reflux condenser, a Teflon paddle stirrer, and a nitrogen gas inlet. Then, St ( $5.8 \times 10^{-2}$  mol), NIPAAm ( $6.0 \times 10^{-3}$  mol), and KPS ( $7.4 \times 10^{-4}$  mol) were added. A steam of nitrogen replaced the air in the flask and the mixture was kept under nitrogen until polymerization was finished. The system was first irradiated for 90 s under 650 W power, and the reaction system could be initiated at 70°C. Then, the temperature of the reaction mixture was kept at 70°C by 130 W. Stable poly(St-co-NIPAAm) dispersion was obtained after the polymerization was carried out at the stirring rate of 350 rpm for 1 h.

### Preparation of self-assembled poly(St-co-NIPAAm) films

The self-assembled poly(St-co-NIPAAm) films were prepared by deposition of the poly(St-co-NIPAAm) particles induced by the capillary forces on the glassware wafer substrates. The production conditions of self-assembled poly(St-co-NIPAAm) films were depicted as follows: The glassware wafers with the diameter of 13 mm were pretreated in a H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (7:3 v/v) mixture solvent for 30 min to create clean surfaces, followed by abundant washing with deionized water. The cleaned glassware wafers were dried in vacuum, which were used as the self-assembled substrates. Then, the cleaned glassware wafers were horizontally placed on the culture dish. The poly(St-co-NIPAAm) dispersions were diluted with deionized water, and the solid content of diluted samples was controlled at 1–2 wt %. The diluted poly(St-co-NIPAAm) dispersions were dipped on the glassware substrates. The samples were deposited for 7–8 days at ambient temperature. In the progress, the capillary forces occurred during water vaporization, and so poly(St-co-NIPAAm) particles were induced by the

capillary forces to self-assemble and form the ordered two-dimensional films on the glassware wafer substrates.

### Scanning electron microscopy

The morphology, size, and size distribution of poly(St-co-NIPAAm) particles were characterized by scanning electron microscopy (SEM) (HITACHI X-650 Scanning Electron Microanalyzer). The samples characterized by SEM were prepared as follows: The obtained poly(St-co-NIPAAm) dispersions were diluted with deionized water. The diluted poly(St-co-NIPAAm) dispersions were coated on the aluminum sample stubs, and then dried in vacuum. After poly(St-co-NIPAAm) particles assembled and arranged in orderly fashion on the aluminum sample stubs, the samples were sputter-coated with gold. The SEM images were obtained at 25°C with Scanning Electron Microanalyzer instrument. The diameters of more than 100 particles were measured from the SEM images, the number average diameter  $D_n$ , weight average diameter  $D_w$ , and the polydispersity index (PDI) were calculated with the eqs. (1)–(3), where  $N_i$  is the number of particles having diameter  $D_i$ .

$$D_n = \frac{\sum_{i=1}^k N_i D_i}{\sum_{i=1}^k N_i} \quad (1)$$

$$D_w = \frac{\sum_{i=1}^k N_i D_i^4}{\sum_{i=1}^k N_i D_i^3} \quad (2)$$

$$\text{PDI} = D_w / D_n \quad (3)$$

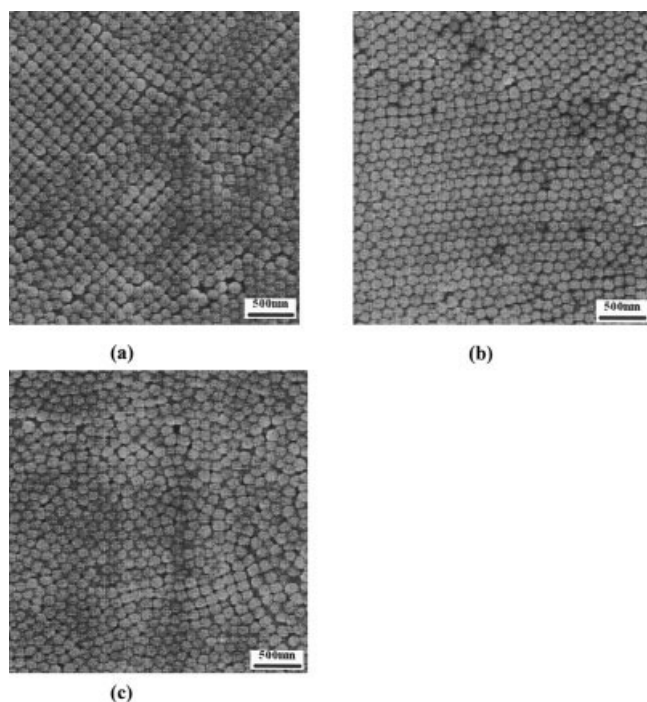
### Atom force microscopy

The self-assembled poly(St-co-NIPAAm) films were prepared with the capillary forces method, as described earlier. The morphologies of the ordered two-dimensional poly(St-co-NIPAAm) films were observed using the TappingMode™ atom force microscopy (AFM) (Nanoscope III<sub>a</sub>, Digital Instruments Metrology Groups), at 25°C. The effects of NIPAAm concentrations on the surface morphologies of the formed poly(St-co-NIPAAm) films were mostly studied.

## RESULTS AND DISCUSSION

### Morphology of poly(St-co-NIPAAm) particles

SEM photographs of poly(St-co-NIPAAm) particles produced by emulsifier-free emulsion polymerization with microwave irradiation, at different NIPAAm concentration, are shown in Figure 1.



**Figure 1** SEM photomicrographs of poly(St-co-NIPAAm) particles prepared with different NIPAAm concentration (a) 0.029 mol/L; (b) 0.048 mol/L; and (c) 0.086 mol/L.

As shown in Figure 1, poly(St-co-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation are spherical morphologies with narrow distribution and poly(St-co-NIPAAm) particles assembled and arranged in orderly fashion on the aluminum sample stubs. The values of  $D_n$ ,  $D_w$ , and PDI of poly(St-co-NIPAAm) particles prepared with different NIPAAm concentration are listed in Table I.

As shown in the Figure 1 and Table I, the characterized results illustrate that the poly(St-co-NIPAAm) particles prepared by emulsifier-free emulsion polymerization with microwave irradiation exhibit narrow distribution, and with the NIPAAm concentration increased from 0.029 mol/L to 0.086 mol/L, the sizes of poly(St-co-NIPAAm) particles decreased slightly. When the PDI values of the particles are very small, the particles could assemble and array in very orderly structures on the substrates.<sup>16</sup> From the results characterized by SEM, the obtained poly(St-co-NIPAAm) particles were induced by capillary forces to self-assemble, and the poly(St-co-NIPAAm) particles arrayed in orderly fashions on the substrates. Moreover, two different array fashions can be observed [square arrays in Fig. 1(a) and hexagonal arrays in Fig. 1(b)], which are similar to the results reported by Cong and Cao.<sup>11</sup>

#### Self-assembled poly(St-co-NIPAAm) films and morphology of films affected by NIPAAm concentration

After the diluted poly(St-co-NIPAAm) dispersions with the solid content of 1–2 wt % were dipped on the

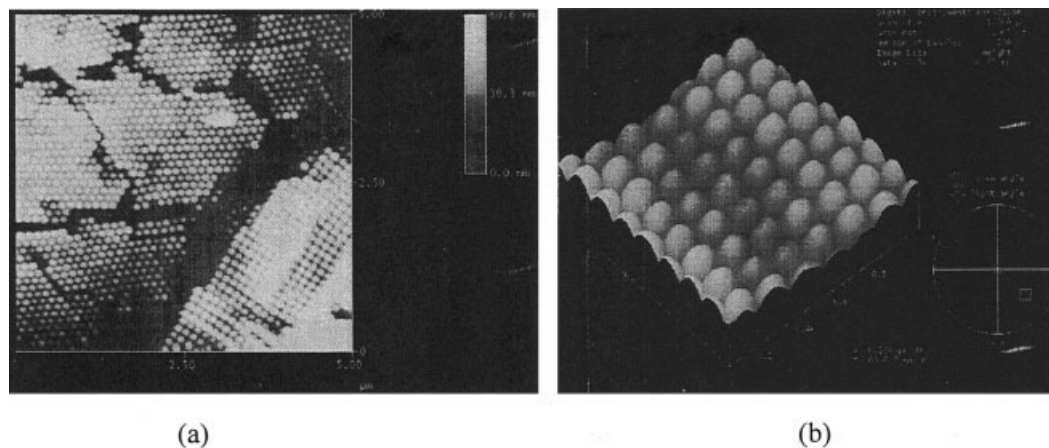
clean glassware wafer substrates in the culture dish, the monodisperse poly(St-co-NIPAAm) particles could be induced by capillary forces to arrange in orderly fashions on the glassware wafer substrates, and form highly ordered two-dimensional films. The formed two-dimensional films could be characterized through AFM.<sup>17</sup> The height image of the two-dimensional poly(St-co-NIPAAm) films characterized by AFM at the scanning range of  $5 \mu\text{m} \times 5 \mu\text{m}$  is shown in Figure 2(a), the three-dimensional perspectives of the self-assembled poly(St-co-NIPAAm) films at the scanning range of  $1 \mu\text{m} \times 1 \mu\text{m}$  is shown in Figure 2(b).

As shown in results characterized by AFM at the different scanning range (Fig. 2), the monodisperse poly(St-co-NIPAAm) particles could self-assemble to array in orderly fashions on the substrates at the different areas. In Figure 2(a), the hexagonal arrays of poly(St-co-NIPAAm) particles could be found; otherwise, the square arrays of poly(St-co-NIPAAm) particles [Fig. 2(b)] could be also observed by AFM. So it could be concluded that the monodisperse poly(St-co-NIPAAm) particles could be induced by capillary forces and arrayed in two different array fashions to form highly ordered two-dimensional films on the clean glassware wafers substrates.

Figure 3 shows the effects of NIPAAm concentration on the morphologies of the self-assembled poly(St-co-NIPAAm) films. The AFM images at different scanning ranges show that the poly(St-co-NIPAAm) particles are arranged in orderly fashions to form highly ordered two-dimensional films, but the surface undulations or surface defective regions of the two-dimensional films have appeared gradually with the NIPAAm concentration increasing. As shown in the Figure 3(a), poly(St-co-NIPAAm) particles prepared at NIPAAm concentration of 0.029 mol/L could arrange in orderly fashion at a larger area; the same results could be also observed at a smaller area [Fig. 3(b)]. When the NIPAAm concentration was increased to 0.086 mol/L, the surface undulations or surface defective regions of the two-dimensional film were very remarkable on the film [Figs. 3(e) and 3(f)]. The results illustrated that there would appear some defects on the surfaces of the formed films prepared at higher NIPAAm concentration.

**TABLE I**  
Diameters of Particles Prepared with Different NIPAAm Concentration

Sample	NIPAAm (mol/L)	SEM		
		$D_n$	$D_w$	PDI
a	0.029	149.0	149.2	1.0013
b	0.048	147.2	147.5	1.0020
C	0.086	135.6	135.9	1.0022



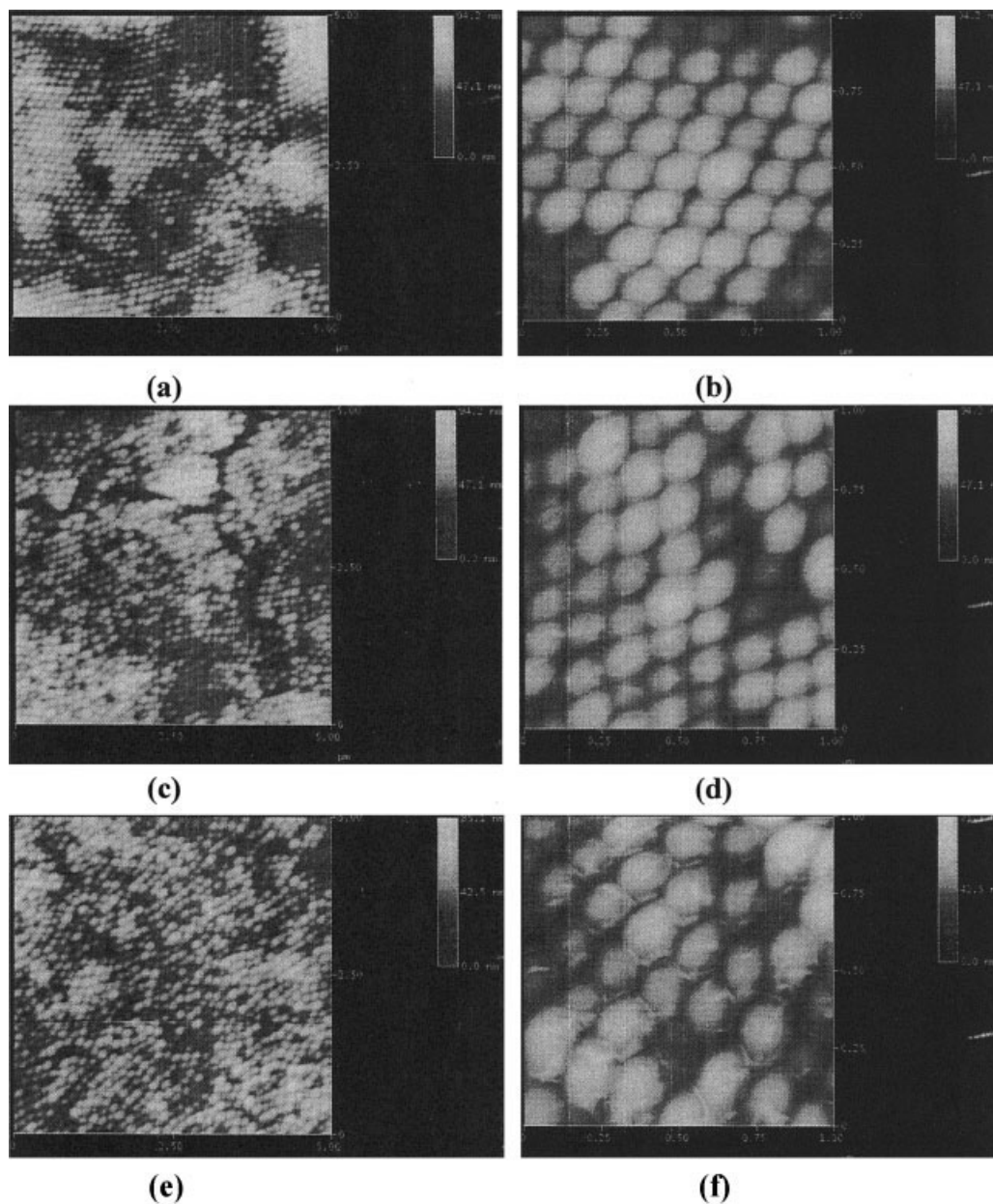
**Figure 2** AFM images of poly(St-co-NIPAAm) films prepared by self-assembly. (a) Height image at the scanning range of  $5 \mu\text{m} \times 5 \mu\text{m}$ . (b) Three-dimensional perspectives of the films at the scanning range of  $1 \mu\text{m} \times 1 \mu\text{m}$ .

Denkov et al.<sup>18</sup> proposed the mechanism of the two-dimensional array formation from latex particles on substrates; the array formation followed two-stage mechanism. A “nucleus” of ordered phase was formed at the first stage, and the crystal growth started through directional motion of particles toward the ordered array at the second stage. In the progress of forming the nucleus, the “immersion capillary forces<sup>19</sup>” were the capillary forces between the particles partially immersed in a liquid layer on a solid substrate. Moreover, the immersion capillary forces were very strong, so that the respective energy of capillary attraction could be much larger than the thermal energy,  $k_B T$ . The capillary interaction was determined by the immersion capillary forces during the progress of forming the nucleus. After the nucleus of ordered phase was formed, a convective water flux played the most of the roles in the directional particle motion and carried along the particles toward the ordered phase. During the progress of the formation of two-dimensional films, the different factors such as particle size, concentration, and water evaporation rate, and so forth, affected the array formation.

In the polymerization system, the experimental results showed that the sizes of the obtained poly(St-co-NIPAAm) particles decreased with the increase in NIPAAm concentrations. As we all know that the particle size affected the array formation on the substrates. During the progress of array formation, the menisci were first formed around each larger particle, and so the larger particles would first form the nucleus and then array in orderly fashions on the substrates, while the smaller particles still moved inside the water layer. The menisci were not formed between the smaller particles, and the smaller particles’ motion were not affected by the capillary forces but by the strong Brownian motion. The Brownian motion might create a state of disorder in the system, and so the

regular array of the smaller particles became difficult on the substrates. With the size of the poly(St-co-NIPAAm) particles decreasing, the surface undulations or surface defective region of the two-dimensional films appeared gradually on the substrates.

On the other hand, the NIPAAm that was a hydrophilic monomer polymerized to form hydrophilic PNIPAAm chains, and these hydrophilic PNIPAAm chains usually intended to distribute on the surfaces of the poly(St-co-NIPAAm) particles to provide the stabilization action. However, it was known that the PNIPAAm chains were softer than polystyrene chains. When the amount of PNIPAAm chains in the poly(St-co-NIPAAm) particles was increased, the surfaces of the formed particles became gradually soft. These soft poly(St-co-NIPAAm) particles might not retain the regular spheres, and the deformation of the particles might occur during the self-assembly process induced by capillary forces. Moreover, when the amount of hydrophilic PNIPAAm chains in the poly(St-co-NIPAAm) particles was increased, the hydrophilicity of the poly(St-co-NIPAAm) particles increased, and so the interactions between the hydrophilic poly(St-co-NIPAAm) particles and the water would increase, which would result in the water evaporation rate decreasing. The variation of the water evaporation rate would change the curvature of the liquid menisci between the particles in the nucleus.<sup>18</sup> For instance, the increased water evaporation rate would decrease the level of the water between the particles, increase the curvature of the menisci, and raise the local sucking capillary pressure, which drives the water influx toward the nucleus. When the level of the water between the particles was increased with the water evaporation rate decreasing, the sucking capillary pressure was decreased and the particle convective influx was also decreased, which might lead to complete stopping of the process of ordering and even to disinte-



**Figure 3** AFM images of poly(St-co-NIPAAm) films prepared with different NIPAAm concentration. NIPAAm concentration: (a, b)  $-0.029$  mol/L; (c, d)  $-0.076$  mol/L; (e, f)  $-0.086$  mol/L. Scanned ranges: (a, c, e)  $5\ \mu\text{m} \times 5\ \mu\text{m}$ ; (b, d, f)  $1\ \mu\text{m} \times 1\ \mu\text{m}$ .

gration of the ordered clusters and restoration of the chaotic particle motion. For these reasons, when the NIPAAm concentration was increased, the surface undulations or surface defective region of the two-dimensional poly(St-co-NIPAAm) films gradually appeared on the substrates.

### CONCLUSIONS

The poly(St-co-NIPAAm) particles could be prepared by emulsifier-free emulsion polymerization with microwave irradiation. The results characterized by SEM

showed that poly(St-co-NIPAAm) particles prepared by microwave irradiation were monodisperse. When the diluted poly(St-co-NIPAAm) dispersions were dipped on the glassware substrates, the monodisperse poly(St-co-NIPAAm) particles could be induced by capillary force to self-assemble, and the poly(St-co-NIPAAm) particles could array in hexagonal fashions and square fashions, and form the ordered two-dimensional films on the glassware substrates. With the NIPAAm concentration increasing, the small sizes of the soft poly(St-co-NIPAAm) particles could be formed. After these particles self-assembled on the

substrates, the surface undulations or surface defective region of the two-dimensional poly(St-co-NIPAAm) films gradually appeared on the substrates.

## References

1. Guo, Q.; Arnoux, C.; Palmer, R. E. *Langmuir* 2001, 17, 7150.
2. Fendler, J. *Chem Mater* 1996, 8, 1616.
3. Yamasaki, T.; Tsutsui, T. *Appl Phys Lett* 1998, 72, 1957.
4. Burmeister, F.; Schafle, C.; Mathes, T.; Bohmisch, M.; Boneberg, J.; Leiderer, P. *Langmuir* 1997, 13, 2983.
5. Gates, B.; Lu, Y.; Li, Z. Y.; Xia, Y., *Appl Phys A* 2003, 76, 509.
6. Alfrey, T.; Bradford, E. B.; Vanderhoff, J. W.; Oster, G. *J Opt Soc Am* 1954, 44, 603.
7. Cyganik, P.; Budkowski, A.; Raczowska, J.; Postawa, Z. *Surf Sci* 2002, 507–510, 700.
8. Yin, Y. D.; Lu, Y.; Gates, B.; Xia, Y. N. *J Am Chem Soc* 2001, 123, 8718.
9. Zhao, S. Y.; Lei, S. B.; Chen, S. H.; Ma, H. Y.; Wang, S. Y. *Colloid Polym Sci* 2000, 278, 682.
10. Kralchevsky, P. A.; Denkov, N. D. *Curr Opin Colloid Interface Sci* 2001, 6, 383.
11. Cong, H. L.; Cao, W. X. *Langmuir* 2003, 19, 8177.
12. Yin, Y. D.; Lu, Y.; Xia, Y. N. *J Am Chem Soc* 2001, 123, 771.
13. Chung, Y. W.; Leu, I. C.; Lee, J. H. Hon, M. H. *Appl Phys Mater Sci Process* 2004, 79, 2089.
14. Zhang, W. M.; Gao, J.; Wu, C. *Macromolecules* 1997, 30, 6388.
15. He, W. D.; Pan, C. Y.; Lu, T. *J Appl Polym Sci* 2001, 80, 2455.
16. Tessier, P. M.; Velez, O. D.; Kalambur, A. T.; Lenhoff, A. M.; Rabolt, J. F.; Kaler, E. W. *Adv Mater* 2001, 13, 396.
17. Lin, F.; Meier, D. J. *Langmuir* 1995, 11, 2726.
18. Denkov, N. D.; Velez, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* 1992, 8, 3183.
19. Paunov, V. N.; Kralchevsky, P. A.; Denkov, N. D.; Nagayama, K. *J Colloid Interface Sci* 1993, 157, 100.