Macromolecules ARTICLE

Macromolecules **2009**, *42*, 6147–6151 **6147**
DOI: 10.1021/ma900354u

Poly(styrene-*co*-*n*-butyl acrylate) Nanofibers with Excellent Stability against Water by Electrospinning from Aqueous Colloidal Dispersions

Aleksandar Stoiljkovic,[†] Rajan Venkatesh,[‡] Evgueni Klimov,[‡] Vijay Raman,[‡] J. H. Wendorff, and Andreas Greiner*[,†]

[†]*Philipps-Universität Marburg, Department of Chemistry and Scientific Center of Materials Science, Hans-Meerwein-Str., D-35032 Marburg, Germany, and* [‡]*BASF SE, Polymer Research Division, Carl-Bosch-Str. 38, D-67056 Ludwigshafen, Germany*

Received February 17, 2009; Revised Manuscript Received July 6, 2009

ABSTRACT: Less brittle nanofibers with excellent stability against water can be prepared via electrospinning of dispersions of styrene−acrylate copolymers from an aqueous environment. The versatility of emulsion polymerization technique allows us to tailor a wide range of properties of the dispersed polymer and the subsequent nanofibers. It was shown that the minimum film formation temperature (MFFT) and correspondingly the glass transition temperature (T_g) of the colloidal polymer, which can be varied by changing the composition of the monomers, have to be in the range of processing temperature, resulting in formation of the fibers with homogeneous morphology and good dimensional stability.

Introduction

Electrospinning has become a versatile technique for the preparation of polymer nanofiber nonwovens for many applications.[1] The nanofibers are obtained using an electrical field that creates an electrostatically driven jet of a polymer solution or melt. Although the conditions are mild, the choice of the solvent is crucial as in many cases explosive, flammable, toxic, or corrosive solvents have to be used. In general, solvent stability of electrospun polymer fibers can be enhanced by photo- or thermal cross-linking.[2−11] However, water stability of nanofiber nonwovens is crucial for numerous applications like filters or textiles. A solution for this problem has been recently reported by electrospinning of aqueous dispersions of water-insoluble polymers.[12] The fibers were produced using a formulation of polystyrene particles and a small amount of a water-soluble polymer that was added to provide viscoelasticity to the solution, which is necessary for fiber formation by electrospinning. After obtaining the fibers the template polymer was removed by washing with water. Although similar approaches have been used in electrospinning of colloidal dispersions of water-insoluble objects from aqueous phase, such as carbon nanotubes,[13−20] silica particles,[21] metal compounds like TiO_2[18,19,22−26] and ZrO_2,[27−29] silk,[30−33] viruses,[34,35] or bacteria,[35,36] none of them has used water-insoluble polymer particles to obtain fibers directly from aqueous phase, which would be stable after removing the template polymer. The use of the template polymer in all of these contributions was limited to an integration of water-insoluble objects into electrospun fibers, where the template polymer was a matrix in which the water-insoluble objects were embedded. Although our concept of preparation of fibers from polystyrene lattices was similar, cohesive interparticle forces that act between closely packed polystyrene particles in the fibers are strong enough to preserve the fiber structure after removing the template polymer. However, electrospun fibers originating from polystyrene formulations display poor mechanical integrity.

The poor mechanical integrity of the so far prepared latex-based fibers from polystyrene lattices is a major drawback for utilization of these fibers. The poor integrity is obviously due to the fact that the particle morphology was preserved in the fibers. Therefore, the goal of this work was the investigation of electrospinning of formulations based on aqueous polymer dispersions, which allow the formation of nonwovens with higher integrity by use of lattices which have a lower minimal film formation temperature (MFT) which is related to the T_g of the polymers used. With this we expect that latex-based nanofiber nonwovens become more useful in applications such as filtration or textiles.

Experimental Section

Materials. Aqueous poly(styrene-*co*-*n*-butyl acrylate) (PSBA), polystyrene (S), and poly(*n*-butyl acrylate) (PBA) latex dispersions were prepared using emulsion polymerization at BASF SE. The T_g (DSC) and average particle size (HDF) samples are summarized in Table 1. Poly(vinyl alcohol) (PVA) (MOWIOL 28−99, M_w = 145 kg/mol, 99% hydrolyzed) was purchased from Kuraray Specialties Europe KSE GmbH. The polymer was used without further purification.

The final formulations for electrospinning were prepared by mixing a certain amount of an aqueous latex dispersion with water-soluble template polymer (PVA) at room temperature. The amount of template polymer is always calculated as parts per hundred of the entire solids (polymer particle + template polymer) in the formulation.

Electrospinning of Formulations. The syringe electrospinning setup has been described previously.[37] A 0.3 mm diameter needle was used as an upper electrode where positive potential was provided by a high-voltage power supply (0−30 kV). A flat counter electrode was positioned 20 cm below the upper electrode and was connected to the high-voltage power supply. A piece of aluminum foil or a metal net placed on the counter electrode was used as collecting substrates. The flow rate of dispersions was about 0.7 mL/h. The applied voltage has been varied between 15 and 60 kV. To obtain oriented fibers, a rotating drum was used as a counter electrode. The rotational speed of the drum was 2500 rpm.

Measurements. *Tensile Test of Fiber Mats.* Tensile measurements and determination of *E* modulus of fiber mats were

---

*Corresponding author. E-mail: greiner@staff.uni-marburg.de.

Table 1. Parameters of Aqueous Dispersions of Particles

sample name	polymer/copolymer	particle diameter, nm	T_g, °C	solid content, wt %
S170	polystyrene	170	~100	40
PSBA153	poly(styrene-*co*-*n*-butyl acrylate)	153	25	50
PSBA102	poly(styrene-*co*-*n*-butyl acrylate)	102	30	40
PSBA7	poly(styrene-*co*-*n*-butyl acrylate)	131	7	40
PSBA27	poly(styrene-*co*-*n*-butyl acrylate)	137	27	40
PSBA64	poly(styrene-*co*-*n*-butyl acrylate)	149	64	40
PBA-50	poly(*n*-butyl acrylate)	85	~−50	40

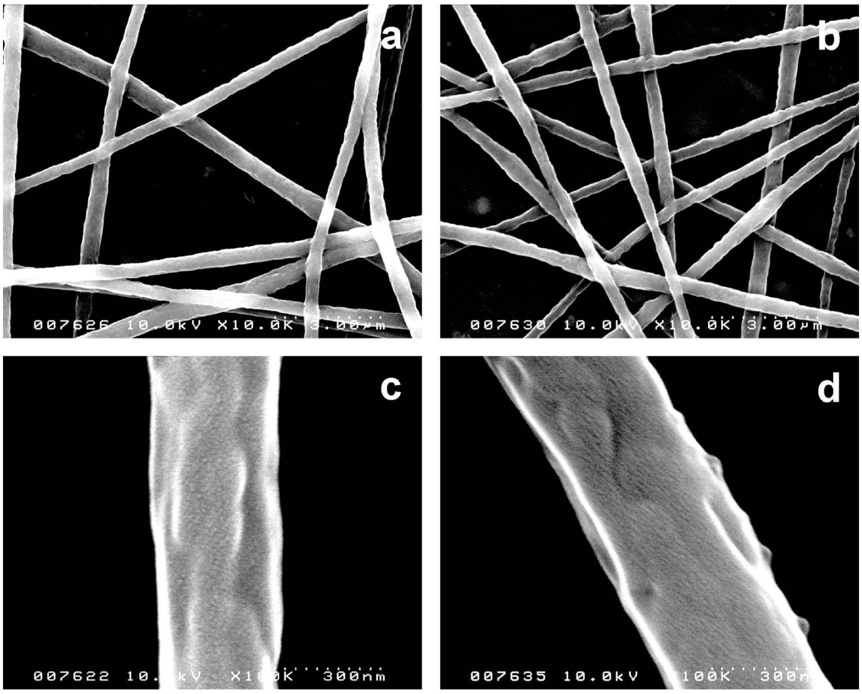

Figure 1. SEM images of fibers obtained by elecrospinning from the dispersion of PBSA153 in 6 wt % aqueous solution of PVA prior to/after water treatment for 16 h: (a, b) low magnification and (c, d) high magnification.

performed on a Minimat microtensile tester (Polymer Laboratories, Ltd., Loughborough, UK). Force−strain curves were recorded, and subsequently, they were used to determine *E* moduli of samples. The sample length was 10 mm, and the displacement of a sample was 5 mm. The samples were stretched at 20 °C temperature with a speed of 0.2 mm/min.

From a fiber mat collected on metal nets were cut out specimens with dimensions 30 × 10 mm^2. The fibers were removed carefully from the metal net and were used in the tensile measurements. At least five samples had been measured before the average values of *E* modulus were calculated. The fibers were measured without removing the template polymer. The collecting time for each fiber mat was 15 min. The weight of the fibers was determined by measuring the weight of the metal parts with and without fibers. Having information about the specimen weight, the dimensions of the specimen and the density of a given polymer/copolymer, a cross-sectional area of the sample could be evaluated. However, it was supposed that all samples had compact cross sections. This assumption did not correspond to the real situation, since fiber mats are very porous structures. This implied that the results obtained by this method did not represent the real mechanical properties of fibers or fiber mats; however, they could be used for comparison of the mechanical properties of the fiber mats prepared in a similar manner. Fiber order parameters where θ is the angle that an individual fiber forms with preferred direction were determined by the equation $S = \langle(3\cos^2\theta - 1)/2\rangle$. The S parameter was determined by measuring the angle of 25 fibers. S is 0 for isotropic orientation and 1 for a perfect alignment of fibers.

Electron Microscopy. Morphology of the fibers was observed with a scanning electron microscope (SEM, model Hitachi S-4100 with accelerating voltage of 5 and 10 kV).

Surface Tension, Viscosity, and Electrical Conductivity. Surface tension measurements were performed at 20 °C on a Dataphysics DCAT 11 tensiometer equipped with an extremely accurate balance. Electrical conductivities were measured at 20 °C using a conductometer inoLab Cond Level 3 with a detector TetraCon 325. Solution viscosities were measured at 20 °C using a rheometer HAAKE PK 100.

Results and Discussion

Effect of MFFT/T_g. The concept of preparation of the water-stable submicrometer fibers from aqueous colloidal dispersions of polymer particles by electrospinning consists of three important steps: (a) preparation of spinnable formulation containing polymer particles of water-insoluble polymer and of a water-soluble template polymer (e.g., PVA), (b) electrospinning of the formulation, where the role of the water-soluble polymer is to increase the entanglements in the water phase and to align the particles in the jet which eventually forms fiber, and the final step (c) comprising the particle interdiffusion as the water evaporates. We believe that the third step should be analogues to the film formation process well-known for polymer latexes/dispersions coated on a substrate. To obtain a continuous homogeneous film, polymer chains of particles should have certain mobility in order to interdiffuse. This ability depends on the minimum film formation temperature (MFFT) of polymeric material. For acrylate- and styrene-based copolymers, the MFFT is related to glass transition temperature (T_g).[38] For elastomeric systems, where cross-linking between chains is realized either by covalent bonds (butadiene) or H-bonding (polyurethane), MFFT is one of the indicator for the film quality.

The concept was applied to a formulation consisting of an aqueous dispersions of particles of the copolymer of styrene and *n*-butyl acrylate with T_g of 25 °C/particle size of 153 nm and PVA as template polymer (6 wt % aqueous solution of PVA; particles:PVA = 80:20). The obtained fibers are shown in Figure 1. The fibers exhibited an excellent stability against water. No differences in the fiber morphology between the fibers prior to and after the removal of PVA could be observed after 16 h treatment in water. Furthermore, the particles could not be recognized in the fibers, indicating their deformation and merging during the process of electrospinning. The average diameter of the fibers was 440 nm.

Determination of Young's modulus of the fiber mats demonstrated a significant improvement of mechanical properties of PSBA fibers regarding to fibers consisting of S particles. The mechanical parameters of fiber mats are summarized in Table 2. Young's modulus of PSBA fiber mats was almost 1 order of magnitude higher than the modulus of S fibers. Naturally, the oriented fibers mats of PSBA153 fibers had even higher modulus of elasticity. SEM images of the measured mats are shown in Figure 2.

In order to further investigate the concept, dispersions consisting of statistical styrene−acrylate copolymers with variable T_g and hence MFFT (see Table 1) by varying the composition of styrene and acrylate in a particle were prepared in the aqueous solution of PVA (6 wt %).

Fiber mats were then analyzed with respect to their morphology. Figure 3 shows electron microscopy micrographs of fiber structures prepared from polymeric materials with different T_g before and after water treatment. With increasing T_g of polymer by increasing a portion of styrene in the particles, the tendency to form a continuous film was less pronounced. The fibers formed from particles with T_g of 64 °C (Figure 3g) displayed particular morphology similar to fibers made of pure polystyrene particles.[2] The influence of T_g of polymer particles was even more pronounced after water treatment (Figure 3b,d,f,h). By decreasing the film forming tendency of the particles with increasing T_g, the stability of the fibers against water was significantly disrupted. Polymer fibers with highest T_g of 64 °C could not keep their integrity because of absence of molecular interdigitation of polymeric chains between particles (Figure 3h). The optimal performance between the film formation tendency, the stability against water and plasticizing effect was displayed by fibers made from particles with T_g of 27 °C (Figure 3 e,f). Thus, polymeric materials with T_g in the range of the temperature at which the electrospinning is performed are preferred. By combination of various monomers in emulsion polymersation, the T_g (MFFT) can be precisely tailored. Materials with

Table 2. Mechanical Properties of Fiber Mats

	S170 nonwoven mats	PSBA153 nonwoven mats	PSBA153 oriented mats
E modulus, MPa	1.2	9.0	31.0
diameter of fibers, nm	680	440	450
diameter of particles, nm	170	153	153
orientation order parameter *S*	0	0	0.9

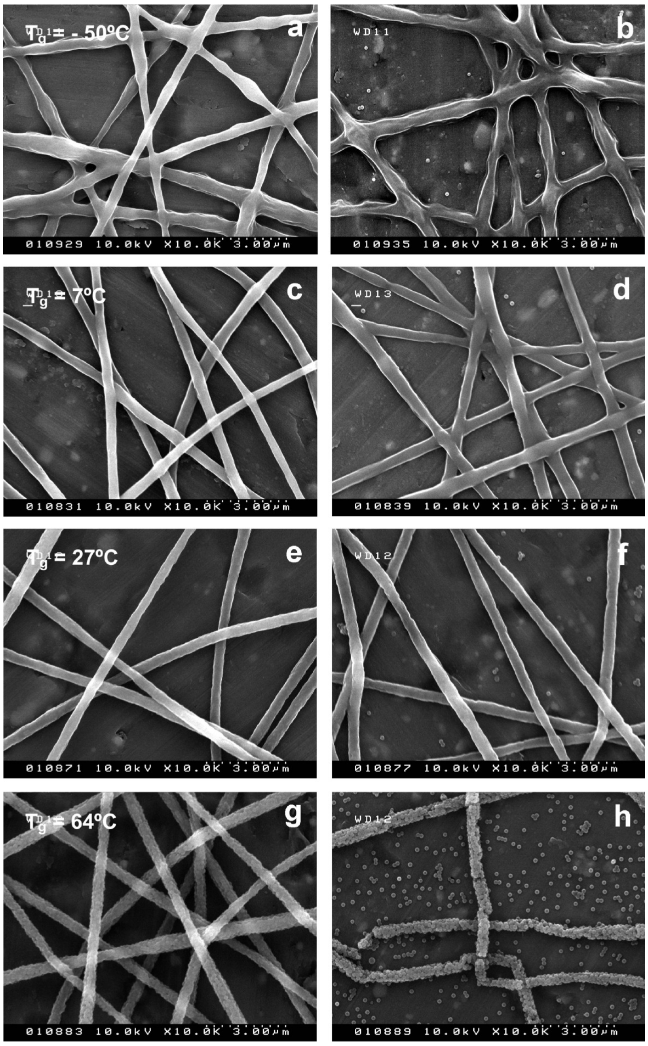

Figure 3. SEM micrographs of fiber structures obtained by electrospinning from dispersions (latex:PVA = 80:20) with different T_g prior to (left) and after (right) water treatment for 16 h: (a, b) PBA-50, (c, d) PSBA7, (e, f) PSBA27, and (g, h) PSBA64.

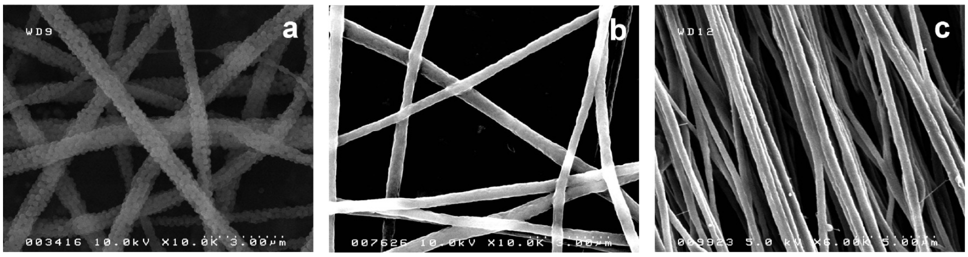

Figure 2. SEM images of fiber mats: (a) S170 nonwoven fiber mat, (b) PBSA153 nonwoven fiber mat, and (c) PBSA153 oriented fiber mat.

Table 3. Average Fiber Diameters

	5.0 wt % PVA PSBA102	5.5 wt % PVA PSBA102	6.0 wt % PVA PSBA102	6.0 wt % PVA PSBA153
diameter of fibers, nm	230	315	350	440

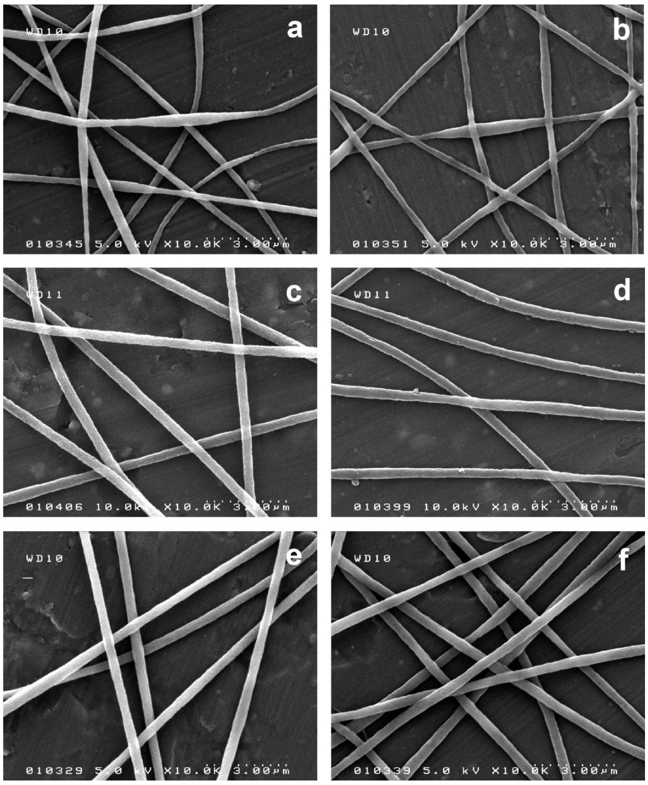

Figure 4. SEM images of fibers obtained by electrospinning from PSBA102 dispersions (PSBA102:PVA = 80:20) prior to/after water treatment: (a, b) 5 wt % PVA, (c, d) 5.5 wt % PVA, and (e, f) 6 wt % PVA.

lower T_g (PBA-50) showed improved mechanical stability compared to styrene as well, however, plastic deformation (flow) dominates their deformation behavior.

Diameter of Fibers. The diameter of fibers is among the most important characteristics of nanofibers. For example, a reduction of the fiber diameter for one-third leads to an increase in the surface area of fibers for 50%. The diameter of fibers obtained from aqueous dispersions by electrospinning was controlled, either via the diameter of particles or via viscosity of dispersions used in the electrospinning process. The average diameter of PSBA153 fibers (particle size 153 nm) was 440 nm, while the average diameter of PSBA102 fibers (particle size 102 nm) was 350 nm although the composition of the dispersions were the same (6 wt % PVA particles:PVA = 80:20) as well as the viscosities of the dispersions (Table 3). Further decrease in the fiber diameter down to 230 nm was achieved by lowering viscosity of dispersions by decreasing amounts of the particles and PVA in the dispersions. The obtained fibers are shown in Figure 4. Too large viscosity drop led to the formation of slightly beaded fibers which average diameter was well below 300 nm.

Conclusions

PSBA fibers with excellent stability against water were successfully prepared by electrospinning from aqueous colloidal dispersions of PSBA particles in the presence of small amounts of PVA. This previously reported concept for the preparation of nanofibers of water-insoluble polymers from water by use of aqueous latex dispersions suffered from the fact that high-T_g lattices, like those based on polystyrene, resulted in rather brittle nanofibers. Here we have shown that nanofibers with obviously less brittleness were obtained when latices based on low-T_g polymers were used in that way that soft PSBA latex particles were deformed during electrospinning. Thereby better contacts between the particles in the fibers have been achieved, resulting in improved mechanical characteristics of nanofibers and outstanding stability against water. As obvious from electromicroscopy, the nanofibers are much smoother as compared to brittle polystyrene-based nanofibers. First measurements of mechanical properties have shown the improvement of mechanical properties of low-T_g particle-based nanofibers versus high-T_g particle-based nanofibers, but for final conclusions measurements on individual fibers will be required, which is the scope of future work. Furthermore, it is obvious that low-T_g polymers may be beneficial for the preparation of smoother and thereby less brittle fibers, but the ulimate disadvantage will be also a lower thermomechanical stability of the fibers which we will address in an upcoming report as well.

Acknowledgment. The authors are indebted to Deutsche Forschungsgemeinschaft for financial support and to BASF AG for the donation of dispersions and financial support.

References and Notes

(1) Greiner, A.; Wendorff, J. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5670–5703.
(2) Zeng, J.; Hou, H.; Wendorff, J. H.; Greiner, A. *e-Polym.* **2004**, No. 078.
(3) Jin, X.; Hsieh, Y.-L. *Polymer* **2005**, *46*, 5149–5160.
(4) Li, L.; Hsieh, Y.-L. *Nanotechnology* **2005**, *16*, 2852–2860.
(5) Jin, X.; Hsieh, Y.-L. *Macromol. Chem. Phys.* **2005**, *206*, 1745–1751.
(6) Ding, B.; Kim, J.; Fujimoto, K.; Shiratori, S. *Chem. Sens.* **2004**, *20* (Suppl. B), 264−265.
(7) Ding, B.; Kim, J.; Miyazaki, Y.; Shiratori, S. *Sens. Actuators, B* **2004**, *101*, 373–380.
(8) Ding, B.; Kim, H.-Y.; Lee, S.-C.; Lee, D.-R.; Choi, K.-J. *Fibers Polym.* **2002**, *3*, 73–79.
(9) Zeng, J.; Hou, J.; Wendorff, J. H.; Greiner, A. *Macromol. Rapid Commun.* **2005**, *26*, 1557–1562.
(10) Choi, S.-S.; Hong, J.-P.; Seo, Y. S.; Chung, S. M.; Nah, C. *J. Appl. Polym. Sci.* **2006**, *101*, 2333–2337.
(11) Stoiljkovic, A.; Agarwal, S. *Macromol. Mater. Eng.* **2008**, *293*, 895–899.
(12) Stoiljkovic, A.; Ishaque, M.; Justus, U.; Hamel, L.; Klimov, E.; Heckmann, W.; Eckhardt, B.; Wendorff, J. H.; Greiner, A. *Polymer* **2007**, *48*, 3974–81.
(13) Dror, Y.; Salalha, W.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. *Langmuir* **2003**, *19*, 7012–20.
(14) Ko, F.; Gogotsi, Y.; Ali, Y.; Naquib, N.; Ye, H.; Yang, G.; Li, C.; Willis, P. *Adv. Mater.* **2003**, *15*, 1161–65.
(15) Salalha, W.; Dror, Y.; Khalfin, R. L.; Cohen, Y.; Yarin, A. L.; Zussman, E. *Langmuir* **2004**, *20*, 9852–55.
(16) Lim, J. Y.; Lee, C. K.; Kim, S. J.; Kim, I. Y.; Kim, S. I. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2006**, *43*, 785.
(17) Wang, G.; Tan, Z.; Liu, X.; Chawda, S.; Koo, J.-S.; Samuilov, V.; Dudley, M. *Nanotechnology* **2006**, *17*, 5829–35.
(18) Hu, G.; Meng, X.; Feng, X.; Ding, Y.; Zhang, S.; Yang, M. *J. Mater. Sci.* **2007**, *42*, 7162–70.
(19) McCullen, S. D.; Stano, K. L.; Stevens, D. R.; Roberts, W. A.; Monteiro-Riviere, N. A.; Clarke, L. I.; Gorga, R. E. *J. Appl. Polym. Sci.* **2007**, *105*, 1668–78.
(20) Jeong, J. S.; Moon, J. S.; Jeon, S. Y.; Park, J. H.; Alegaonkar, P. S.; Yoo, J. B. *Thin Solid Films* **2007**, *515*, 5136–41.

(21) Lim, J.-M.; Moon, J. H.; Yi, G.-R.; Heo, C.-J.; Yang, S.-M. *Langmuir* **2006**, *22*, 3445–3950.

(22) Li, D.; Xia, Y. *Nano Lett.* **2003**, *3*, 555–560.

(23) Watthanaarun, J.; Pavarajarn, V.; Supaphol, P. *Sci. Technol. Adv. Mater.* **2005**, *6*, 240–245.

(24) Park, S.; Lee, D. Y.; Lee, M.-H.; Lee, S.-J.; Kim, B.-Y. *J. Korean Ceram. Soc.* **2005**, *42*, 548.

(25) Nuansing, W.; Ninmuang, S.; Jarernboon, W.; Maensiri, S.; Seraphin, S. *Mater. Sci. Eng., B* **2006**, *131*, 147–155.

(26) Lee, D. Y.; Kim, B.-Y.; Lee, S.-J.; Lee, M.-H.; Song, Y.-S.; Lee, J.-Y. *Korean Phys. Soc.* **2006**, *48*, 1686.

(27) Jing, N.; Wang, M.; Kameoka, J. *J. Photopolym. Sci. Technol.* **2005**, *18*, 503.

(28) Azad, A.-M.; Matthews, T.; Swary, J. *Mater. Sci. Eng., B* **2005**, *123*, 252–258.

(29) Azad, A.-M. *Mater. Lett.* **2006**, *60*, 67–72.

(30) Jin, H.-J.; Fridrikh, S. V.; Rutledge, G. C.; Kaplan, D. L. *Biomacromolecules* **2002**, *3*, 1233–39.

(31) Wang, M.; Jin, H.-J.; Kaplan, D. L.; Rutledge, G. C. *Macromolecules* **2004**, *37*, 6856–64.

(32) Putthanarat, S.; Eby, R. K.; Kataphinan, W.; Jones, S.; Naik, R.; Reneker, D. H.; Farmer, B. L. *Polymer* **2006**, *47*, 5630–32.

(33) Chen, C.; Chuanbao, C.; Xilan, M.; Yin, T.; Hesun, Z. *Polymer* **2006**, *47*, 6322–27.

(34) Lee, S.-W.; Belcher, A. M. *Nano Lett.* **2004**, *4*, 387–535.

(35) Salalha, W.; Kuhn, J.; Dror, Y.; Zussman, E. *Nanotechnology* **2006**, *17*, 4675–81.

(36) Gensheimer, M.; Brandis-Heep, M.; Thauer, R.; Wendorff, J. H.; Greiner, A. *Adv. Mater.* **2007**, *19*, 2480–82.

(37) Bognitzki, M.; Hou, H.; Ishaque, M.; Frese, T.; Hellwig, M.; Schwarte, C.; Schaper, A.; Wendorff, J. H.; Greiner, A. *Adv. Mater.* **2000**, *12*, 637–640.

(38) Schwartz, M.; Baumstark, R. Waterbased acrylates for decorative coatings. In *Emulsion Polymerisation and Emulsion Polymers*; Lovell, P., El-Aasser, M., Eds.; Wiley: New York, 2001.