Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 3974–3981

polymer

www.elsevier.com/locate/polymer

Preparation of water-stable submicron fibers from aqueous latex dispersion of water-insoluble polymers by electrospinning

Aleksandar Stoiljkovic [a], Michael Ishaque [b], Uwe Justus [a], Lisa Hamel [a], Evgeni Klimov [b], Walter Heckmann [b], Bruno Eckhardt [c], Joachim H. Wendorff [a], Andreas Greiner [a,*]

[a] *Philipps-Universität Marburg, Department of Chemistry and Scientific Center for Materials Science, Hans-Meerwein-Str., D-35032 Marburg, Germany*
[b] *BASF Aktiengesellschaft, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany*
[c] *Philipps-Universität Marburg, Department of Physics, Renthof 6, D-35032 Marburg, Germany*

Received 8 January 2007; received in revised form 13 April 2007; accepted 15 April 2007
Available online 4 May 2007

Abstract

Submicron polystyrene (PS) fibers were prepared by electrospinning of an aqueous dispersion of PS latex and a small amount of poly(vinyl alcohol) (PVA) and subsequent extraction by water. Depending on particle size, surfactant, ratio of PS:PVA, and applied voltage fibers of different morphology and water stability were obtained. Analysis of latex fibers by TEM revealed hexagonal packaging of particles within the fibers.

Keywords: Electrospinning; Nanofibers; Aqueous dispersions

---

1. Introduction

Electrospinning is a versatile method for the preparation of ultrathin polymer fibers. Recently, this method has attracted significant attention due to its manifold options for the preparation of continuous nanofibers. Electrospun fibers can be employed in many possible applications in different fields such as tissue engineering, drug delivery, filtration, textiles, sensors, optical and electronic devices, catalysis, etc [1–3].

The principle of electrospinning is straightforward. A strong electrical field is applied to a droplet of a polymer solution or polymer melt [4–6] formed at the tip of a nozzle acting as an electrode. On the other side, the counter electrode is placed, usually several tens centimeters below the nozzle. During the initial stage of electrospinning the shape of the droplet is turned from spherical to conical due to the charging of the fluid. When an electrical force of the electrical field overcomes surface tension of the droplet, a jet is ejected from the tip of the cone. The jet thins rapidly during its travel to the counter electrode due to electrostatic repulsion between surface charge and due to solvent evaporation. Finally, the solid nanofibers are deposited on the counter electrode.

Various polymers have been electrospun in ultrafine fibers in recent years, mostly from polymer solutions [1–3]. Organic solvents, as well as water, can be used as a solvent depending on the solubility of the polymer in use. From an environmental and safety point of view water as a solvent is preferred but the electrospun fibers from water-soluble polymers, such as poly(vinyl alcohol) (PVA) or poly(ethylene oxide) (PEO) dissolve readily in water, which is a major drawback for their use in technical applications such as textiles and filtration.

The water stability of electrospun fibers of water-soluble polymers can be improved significantly by crystallization or by chemical crosslinking. For example, the water stability of electrospun PVA fibers was enhanced considerably by solvent treatment with methanol [7], by crosslinking with poly(acrylic acid) [8,9] or photocrosslinking of modified PVA [10].

This paper reports on water-insoluble polymer fibers obtained by electrospinning from aqueous dispersions of polymer

---

* Corresponding author. Tel.: +49 6421 2825573; fax: +49 6421 2825785.
E-mail address: greiner@staff.uni-marburg.de (A. Greiner).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.04.050

latex particles, which has not been reported so far to the best of our knowledge. However, it should not remain unmentioned, that several reports are in literature on electrospinning of colloidal dispersions of water-insoluble objects from aqueous phase, for example carbon nanotubes [11–14], silica particles [15], metal compounds like TiO_2 [16–20], ZrO_2 [16,21–23], silk [24,25], viruses [26], and bacteria [27]. All of these contributions have in common that a water-soluble polymer was used to integrate water-insoluble objects into electrospun fibers by a kind of gluing together during electrospinning. However, none of these contributions used water-insoluble polymer particles although it would be of great fundamental as well as technical interest to obtain water-insoluble polymer fibers directly from aqueous phase. Furthermore, it will be of interest to learn more about the dynamics of the electrospinning process by investigation of particle arrangement in electrospun fibers. Both issues are in the focus of this contribution. The effects of processing parameters e.g. particle size, composition of dispersions, addition of a non-ionic surfactant and applied voltage on morphology and stability of fibers were investigated. The use of aqueous dispersion for the preparation of water-insoluble fibers by electrospinning offers new perspectives for the preparation of polymer micro- and nanofibers with new morphologies and property profiles and should be therefore of fundamental as well as technical interest.

2. Experimental

2.1. Materials

Aqueous polystyrene latex dispersions were obtained from BASF AG. The diameters of used latex particles were 100 nm (S100), 200 nm (S200) and 335 nm (S335). The solid content of the dispersions was 40 wt%. The average molecular weight of polystyrene was 250,000–300,000 g/mol. All lattices were crosslinked. Basensol (BASF), a block copolymer of propylene oxide and ethylene oxide, was used as a non-ionic surfactant. PVA (Kuraray Specialities Europe KSE GmbH) was used in two grades as MOWIOL 28–99 ($M_w = 145,000$ g/mol, 99% hydrolysed) and MOWIOL 56–98 ($M_w = 195,000$ g/mol, 98% hydrolysed). Polymers were employed without further purification.

Dispersions for electrospinning were prepared by mixing of certain amounts of a latex dispersion and PVA in water (the concentrations from 10 to 15 wt%) at room temperature. A typical composition was 6 wt% PVA (28–99) S:PVA = 80:20 and 1 wt% Basensol. The explanation is as follows: 6 wt% PVA related to water, the weight ratio between S particles and PVA is 80:20 ($m(\mathrm{S}):m(\mathrm{PVA}) = 80:20$) and 1 wt% Basensol related to amount of S particles.

The electrospinning set-up was used as described previously [28]. 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 placed 20 cm below the upper electrode. The negative potential was provided by a high voltage power supply (0 to −30 kV). A piece of Al foil was used as a collecting substrate. The flow rate of dispersion of 0.7 ml/h was controlled by a pump. Temperature and humidity in the electrospinning chamber were measured. Temperature was in the range: 15–18 °C, and humidity: 30–50%. During an electrospinning experiment all parameters were kept constant, except the voltage.

The template polymer PVA was removed from electrospun fibers after electrospinning by water extraction. The standard procedure was as follows: fibers were put in 1 L water for at least 15 h at room temperature. After this treatment fibers were dried in air for 24 h prior to characterization.

2.2. Measurements

Morphology of the electrospun fibers was observed by a scanning electron microscopy (SEM, model Cam Scan 4 with accelerating voltage of 15 kV and model Hitachi S-4100 with an accelerating voltage of 5 and 10 kV) and transition electron microscopy (model JEM 3010 at 300 kV). Surface tension measurements were performed on a Dataphysics DCAT 11 tensiometer. Electrical conductivity of dispersions was measured using a conductometer inoLab® Cond Level 3. Viscosity measurements were carried out on a rheometer HAAKE PK 100 and ARES LS4 shear controlled rheometer. IR spectra were recorded on an IR DIGILAB Excalibur spectrometer with Win-IR Pro Software.

3. Results and discussion

The motivation for the work reported here is driven by the requirement of water-insoluble electrospun fibers from aqueous phase. The concept to solve this problem, which is shown schematically in Fig. 1, is the use of aqueous dispersions of water-insoluble polymers for electrospinning and the exploitation of their tendency for film formation. In order to support fiber-like arrangement of PS latex particles upon electrospinning, a small amount of a water-soluble polymer is added. In the initial state of the fiber formation, the water-soluble polymer acts as a kind of glue or template polymer. According to this concept the water-soluble template polymer can be removed after electrospinning without disintegration of the latex fiber. After the removal of the template polymer, the particles hold together due to the attractive van der Waals' forces, which are acting between the particles in the fibers.

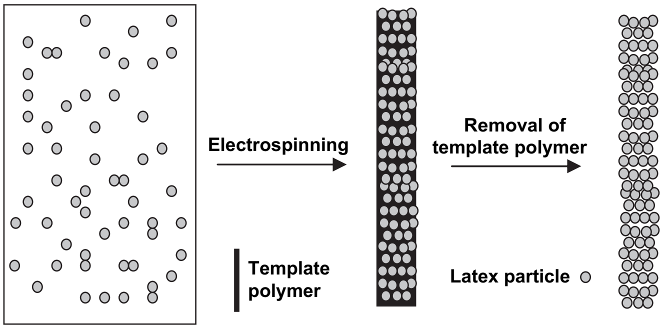

Fig. 1. Schematic description of the latex electrospinning process.

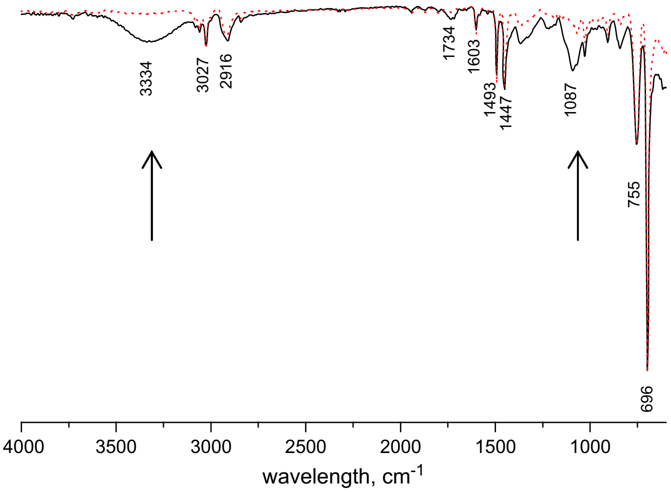

Fig. 2. IR spectra of fibers before (solid line) and after water treatment (dashed line) obtained by electrospinning of dispersion of 6.5 wt% PVA (28–99) S200:PVA = 80:20, 1 wt% Basensol.

In order to verify the concept of latex electrospinning an aqueous PS latex dispersions in combination with PVA was electrospun under standard conditions. The resulting fibers were analyzed by IR spectroscopy prior to and after water treatment (Fig. 2) and by SEM. It was found that the as spun fibers showed characteristic absorption bands of PVA ($\sim 3335\ \text{cm}^{-1}$ O–H stretching, $\sim 1085\ \text{cm}^{-1}$ C–O stretching and O–H bending) and polystyrene (~ 1490 and $1450\ \text{cm}^{-1}$ aromatic C–C stretching, $\sim 750\ \text{cm}^{-1}$ C–H bending, $\sim 700\ \text{cm}^{-1}$ aromatic C–C bending) whereas the fibers after water extraction displayed only the characteristic bands of PS but none of PVA. The extracted fiber remained macroscopically intact and a fiber-like assembly of spherical PS particles (Fig. 3) was revealed by SEM analysis.

3.1. Effect of particle size

Latex particle size influences the fiber formation and the shape of obtained fibers. In order to study this effect, three dispersions were prepared: (1) dispersion with particle size 100 nm (S100), (2) dispersion with particle size 200 nm (S200) and (3) dispersion with particle size 335 nm (S335).

To probe the integrity of the electrospun fibers obtained by electrospinning of the dispersions and to remove the template polymer, the fibers were placed in 1 L of water for 16 h at 20 °C. The morphology of the fibers prior to and after water treatment was analyzed using SEM. The SEM pictures of the fibers are shown in Fig. 4.

Increasing the particle size resulted in fibers, which disintegrated after the removal of the template polymer (Fig. 4d and f). The fibers, which retained their shape, were the fibers made from S100 (Fig. 4b). These fibers preserved their shape after water treatment indicating their stability in comparison to fibers made from particles whose sizes were 200 and 335 nm.

To explain the influence of size on the stability of the fibers, the average diameter of fibers and the range of fiber diameters were measured. The average diameter of fibers prior to the water treatment, the range of fiber diameters as well as the ratio between the average diameter of the fibers and the diameter of particles are summarized in Table 1.

The average diameter of S100 fibers was 420 nm and the range was between 280 and 500 nm. A more important parameter was certainly the ratio between the average diameter of fibers and the average diameter of the particles. In this case the ratio was 4.2. It points to a relative compact packing of the particles in the fibers. As a consequence, the S100 fibers showed the best water stability among the obtained fibers.

On the other hand, the SEM pictures revealed that S200 and S335 fibers were not stable. The average diameter of S200 fibers was 320 nm and the average diameter of S335 fibers was 475 nm. However, the ratios between the average diameter of fibers and the average diameter of particles were 1.6 and 1.4, respectively, and they were relatively close to unity. When the ratio between the average diameter of fibers and the average diameter of particles is 1, the particle size and the average diameter of fibers are equal and the fibers consist of particles arranged in a single row. Such structures are not of particular stability. The range of fiber diameters showed for S200 and S335 fibers that there were fibers (more precisely the parts of fibers) whose diameters were below the average particle

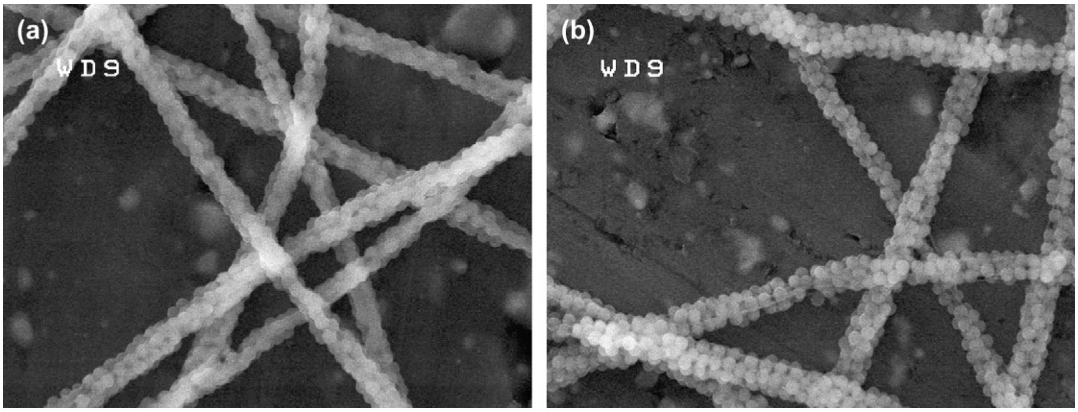

Fig. 3. SEM micrograph of fibers before (a) and after water treatment (b) obtained by electrospinning of dispersion of 6.5 wt% PVA (28–99) S200:PVA = 80:20, 1 wt% Basensol. The length of the horizontal edge corresponds to 8 μm.

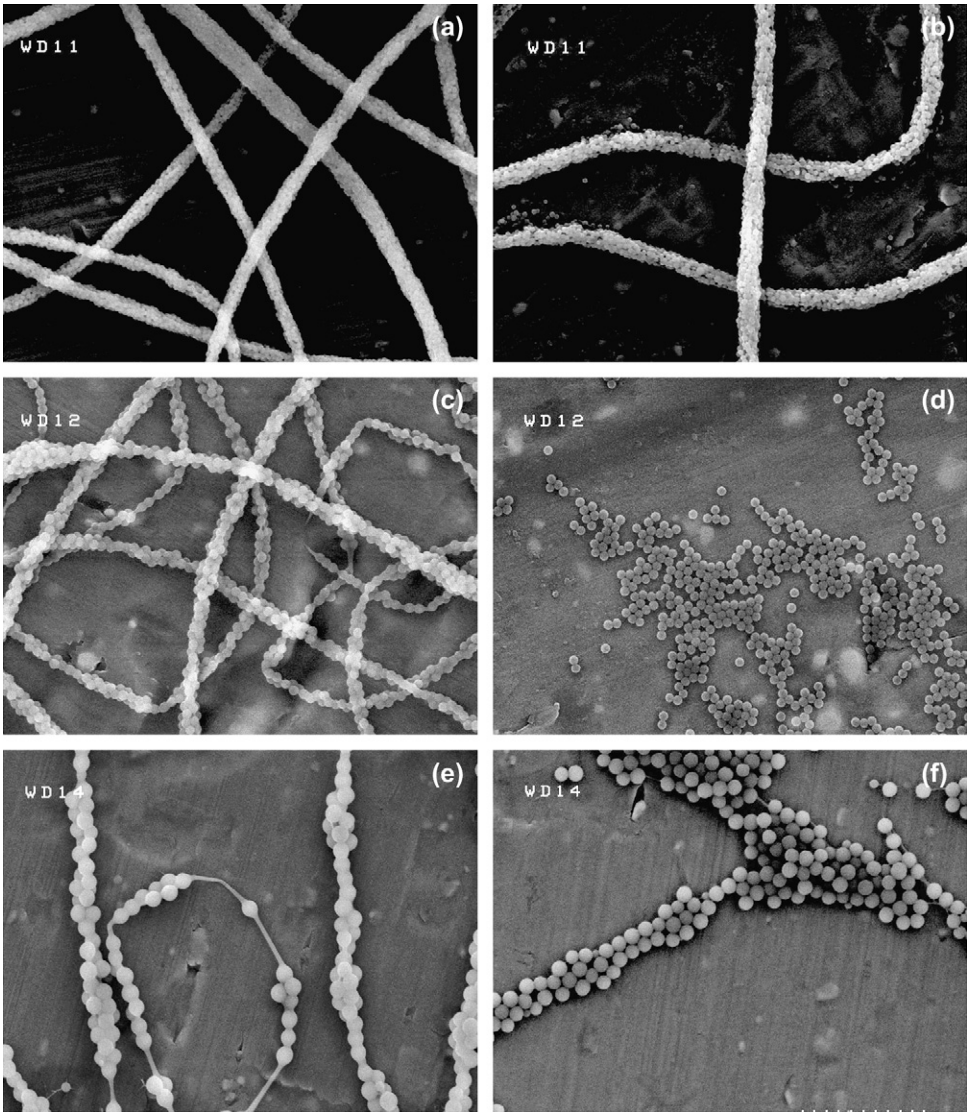

Fig. 4. SEM images of fibers obtained by electrospinning from dispersion (6 wt% PVA (28–99) S:PVA = 80:20, 30 kV) of different particle sizes before/after water treatment: S100 (100 nm, a/b), S200 (200 nm, c/d), and S335 (335 nm, e/f). The length of the horizontal edge corresponds to 12 μm.

Table 1
The average diameter of fibers

	Particle diameter, nm (d)	Average diameter of fibers prior to water treatment, nm (D)	Range, nm	D/d
S100	100	420	280–500	4.2
S200	200	320	150–650	1.6
S335	335	475	100–900	1.4

size. These fibers represented the PVA parts where the particles were not present. Immersing these fibers in water and dissolving the template polymer resulted in the disintegration of the fibers.

3.2. *Effect of non-ionic surfactant*

Usually, the surface of polymer particles is covered with an ionic surfactant that improves the stabilization of dispersions through the repulsion of the like-charged particles. That is most likely counterproductive to fiber formation in our case (the repulsive forces hinder the packing of particles in a fiber and in that way influence the stability of fibers). Therefore, the change from ionic (stabilization by charge repulsion) to non-ionic surfactants (stabilization by steric repulsion) could improve agglomeration of particles in course of the fiber formation.

The non-ionic surfactant Basensol was used to replace the ionic surfactant. Dispersions with different amounts of Basensol were prepared (no Basensol, 1, 3, and 5 wt% of Basensol) (Fig. 5). The particle size was 100 nm (S100). No fibers were obtained by electrospinning at the standard conditions used throughout this work (200 mm, 30 kV) from the dispersions without Basensol and with 1 wt% of Basensol. However, it was possible to produce fibers from the dispersion with 3 wt% of Basensol. The fibers were cylindrical, without defects and showed excellent stability after water treatment (Fig. 5b). Increasing the amount of Basensol to 5 wt% resulted in beaded

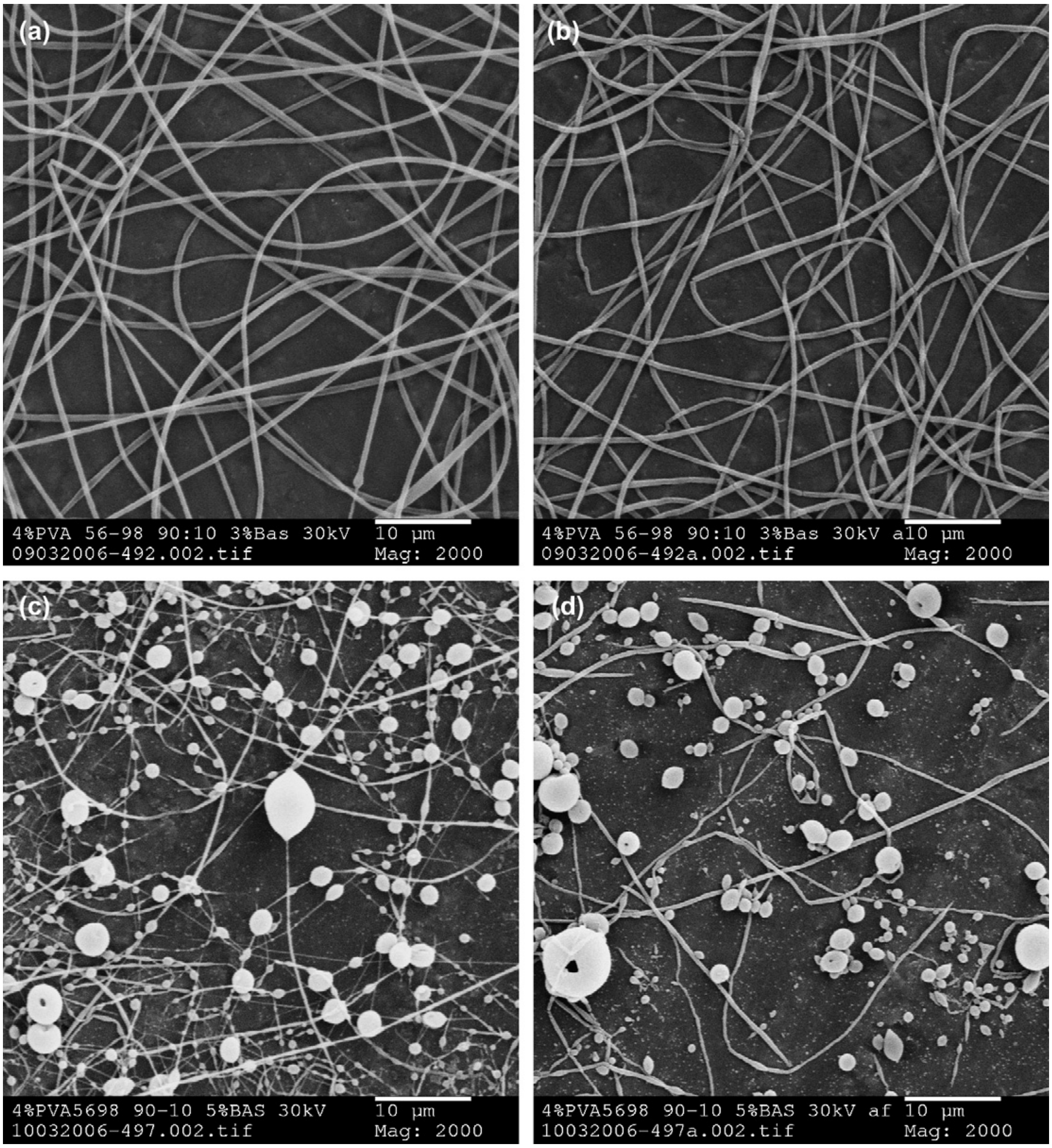

Fig. 5. SEM images of fibers obtained by electrospinning from dispersion (4 wt% PVA (56–98) S100:PVA = 90:10, 30 kV) with different amounts of Basensol before/after water treatment: 3 wt% Basensol (a/b) and 5 wt% Basensol (c/d).

fibers (Fig. 5c) and further addition of Basensol led to the flocculation of the dispersion prior to electrospinning.

3.3. Effect of composition of dispersion

The amount of particles in the fibers is an important factor for the fiber formation from latex dispersions by electrospinning. For that reason, the dispersions with different PVA to S200 ratios (40:60, 60:40 and 80:20) were electrospun. The particle size was 200 nm (S200). The fibers obtained from these dispersions were analyzed by SEM prior and after water treatment (Fig. 6).

Fibers were obtained for all compositions, however, only dispersion with the ratio of S200:PVA = 80:20 remained intact after water treatment (Fig. 6f), whereas the fibers with higher PVA content disintegrated after contact to water (Fig. 6b and d).

3.4. Effect of voltage

The electrical field, characterized by the applied voltage and the distance between the electrodes, can have a significant effect on the fiber formation in electrospinning. The distance between electrodes was kept constant, while the applied voltage was varied between 10 and 40 kV. Fig. 7 shows SEM images of fibers obtained from latex dispersion at 10, 20, 30, and 40 kV.

The fibers electrospun at 10 and 40 kV showed beaded structure (Fig. 7a and g) whereas the fibers at 20 and 30 kV were smooth and without beads (Fig. 7c and e). The stability of electrospun fibers after the removal of template polymer was excellent. The morphology of the created beads at 10 and 40 kV was different. The shape of beads at 10 kV was more spindle-like while the shape of beads at 40 kV was more spherical.

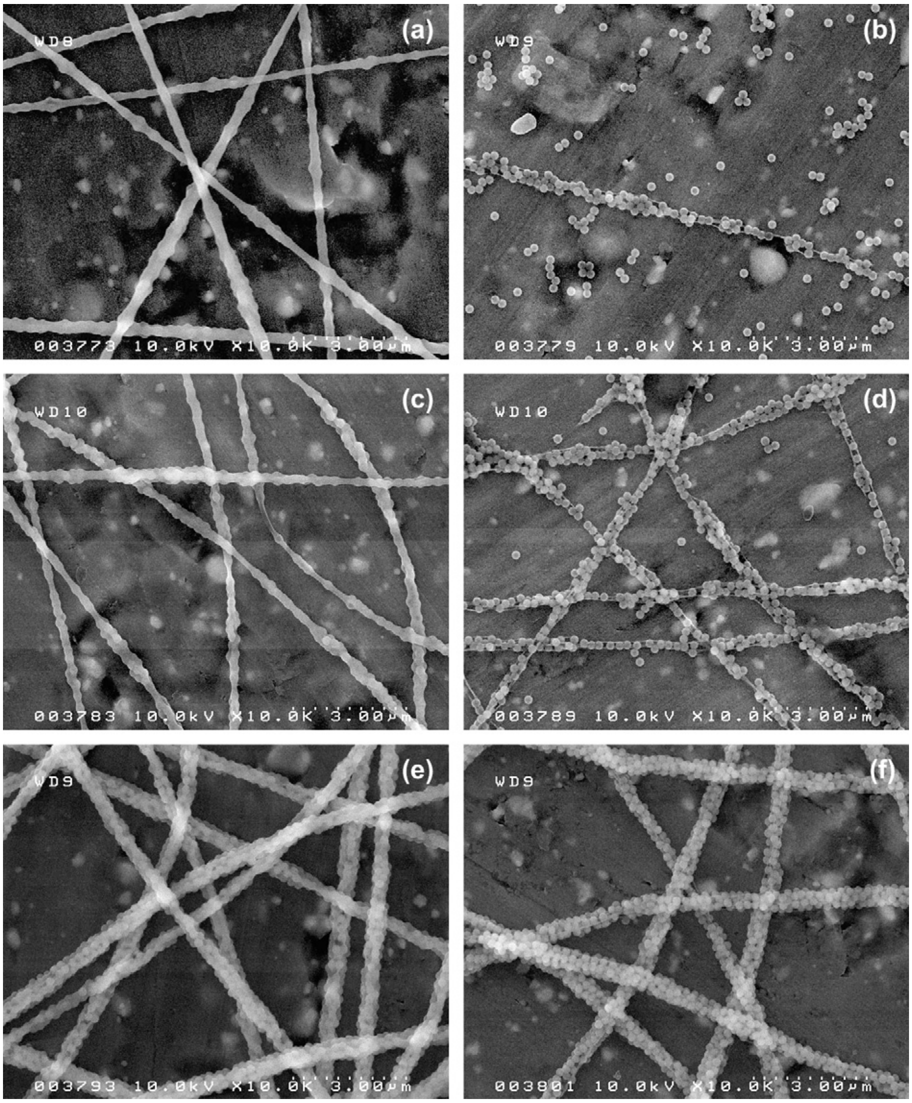

Fig. 6. SEM images of fibers obtained by electrospinning from dispersion (6.5 wt% PVA (28–99) 1 wt% Basenol, 15 kV) with different ratios of PVA to S200 before/after water treatment: 40:60 (a/b), 60:40 ratio (c/d), and 80:20 ratio (e/f). The lengths of the horizontal edge correspond to 12 μm.

The mechanism of bead formation at 10 kV could be explained by using the work of Hohman et al. [29]. They identified three different instability modes of the jet: Rayleigh mode, the axisymmetric conducting mode and the whipping conducting mode. At lower electrical fields, both the axisymmetric modes are stronger than the whipping mode. These axisymmetric instabilities favour the formation of beaded fibers. That was the case when the applied voltage was 10 kV. On increasing the applied voltage the dominant instability was changed from axisymmetric to whipping. The whipping instability favours formation of smooth, bead-free fibers (like in the cases when the applied voltages were 20 and 30 kV). Further increase in the applied voltage led again to the formation of beads.

Deitzel et al. [30] observed similar behaviour of PEO solution in water. They also noticed the increase in number of bead defects present in the fiber mat with increase in the applied voltage. The possibility that axisymmetric modes become dominant again cannot be omitted entirely. It could mean that the net charge density carried by the jet was reduced. However, no evidence of corona discharge (sparks or snaps) during the experiment was noticed.

3.5. Arrangement of particles in fibers

In a dispersion, the particles are stabilized by repulsion and distributed randomly without any order. During the electrospining process the polymer particles come into contact due to the thinning of the jet. SEM and TEM analyses revealed that a certain degree of near order between particles exists in the electrospun fibers. Fig. 8 shows SEM and TEM images of fiber made from S200 particles.

Obviously, the packing of particles into the fibers was not random. Cross-sectional cuts of fibers displayed hexagonal packing of particles (Fig. 9a), although the order of particles in the fibers was not as high as the order in films (Fig. 9b).

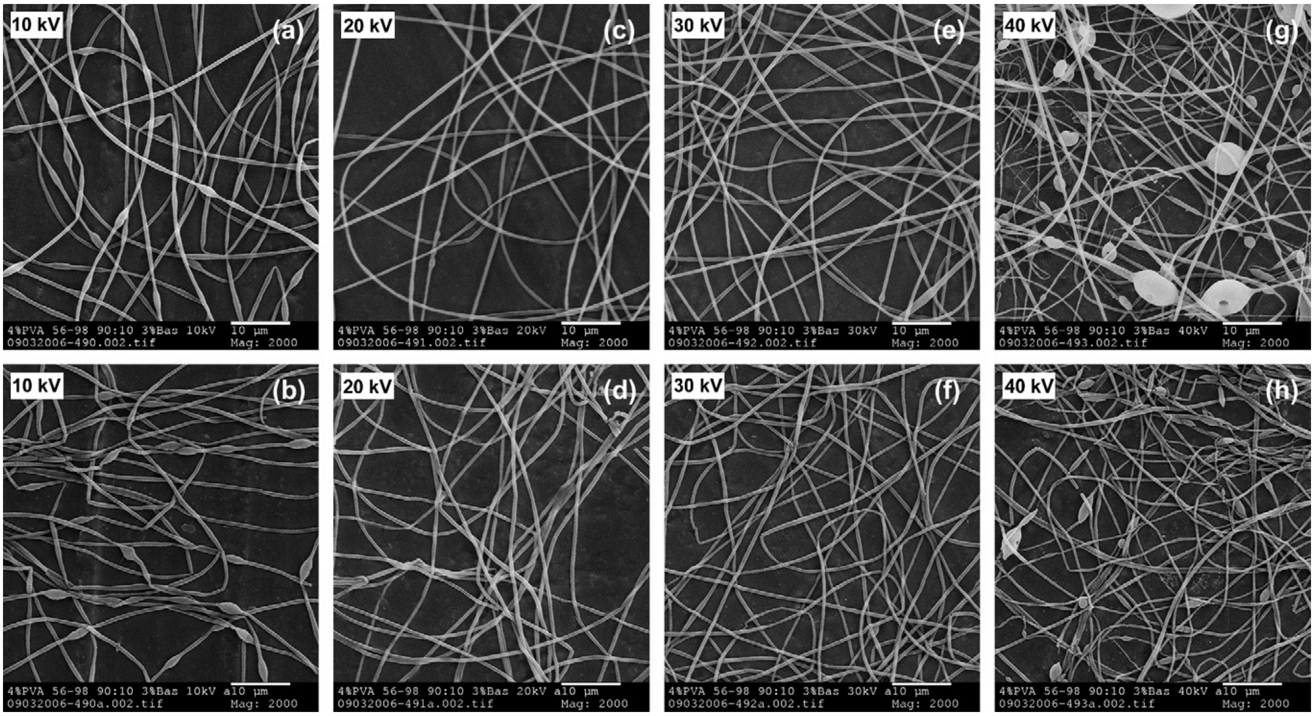

Fig. 7. SEM images of fibers obtained by electrospinning from dispersion (4 wt% PVA (56–98) S100:PVA = 90:10 3 wt% Basensol) at different applied voltages before/after water treatment: 10 kV (a/b), 20 kV (c/d), 30 kV (e/f),and 40 kV (g/h).

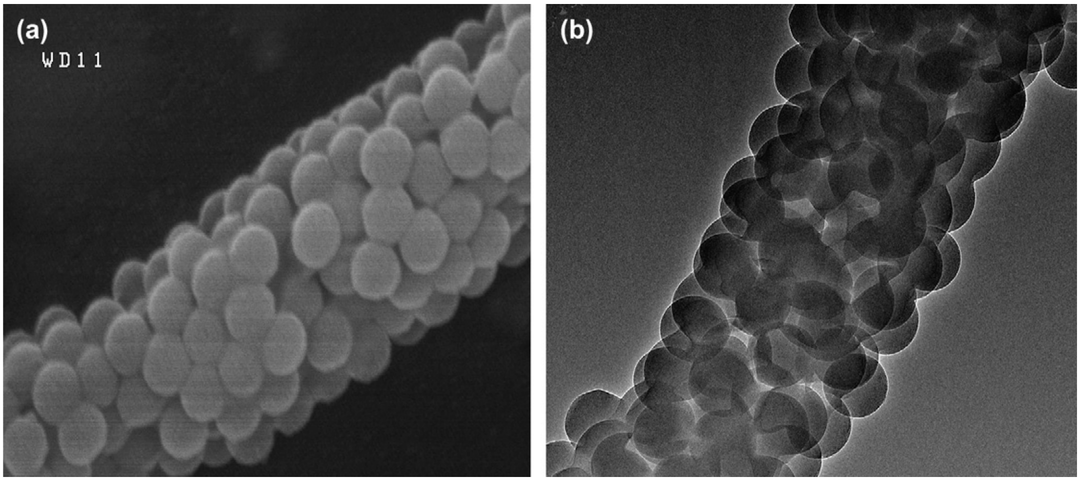

Fig. 8. SEM (a) and TEM (b) images of fibers obtained by electrospinning from dispersion of 6.2 wt% PVA (28–99) S200:PVA = 85:15 3 wt% Basensol, 15 kV. The length of the horizontal edge corresponds to 35 μm and 2 μm.

It is likely, that different time scales at which these two processes take place are the reason for the difference in order. The formation of the fibers by electrospinning occurred within milliseconds, while the formation of the film took several hours.

4. Conclusions

Water-stable submicron fibers of water-insoluble polymers were successfully prepared by electrospinning of aqueous latex dispersions using a small amount of a water-soluble polymer for fiber formation. With proper choice of parameters the fibers remain stable even after extensive water treatment and thereby removal of the water-soluble polymer. No disintegration of fibers was observed which is an important feature for numerous technical applications. Particle size, type of surfactant, composition of dispersion, and applied voltage have a pronounced impact on fiber formation upon electrospinning and stability against water. In general small latex particles, non-ionic surfactants, small amounts of water-soluble polymers, and small voltages were favourable for the system investigated here. Another new and interesting feature of electrospun fibers from latex dispersions is the arrangement of particles in the fibers which opens the perspective for further

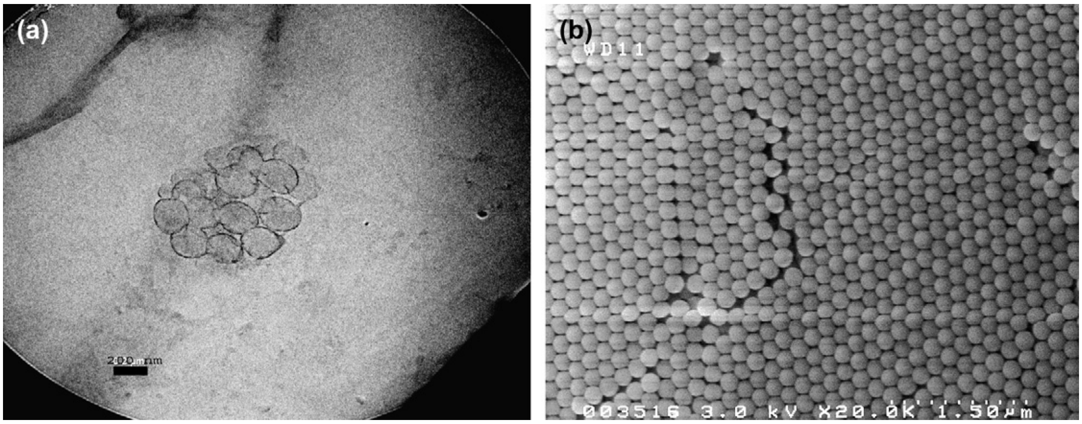

Fig. 9. TEM images of a latex fiber cross-sectional cut obtained by electrospinning from dispersion (6.5 wt% PVA(28–99) S200:PVA = 80:20 1 wt% Basensol, 15 kV, no water extraction) (a) in comparison to a cast film of the same dispersion (40% S200 in water, basic dispersion) (b).

property tuning by ordering/disordering of particles in the fibers. This will also require theoretical analysis, which is presently under way.

Acknowledgment

The authors are indebted to DFG and BASF Aktiengesellschaft for financial support.

References

[1] Greiner A, Wendorf JH. Angew Chem, in press.
[2] Li D, Xia Y. Adv Mater 2004;16:1151–70.
[3] Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. Compos Sci Technol 2003;63:2223–53.
[4] Larrondo L, Manley RSJ. J Polym Sci Phys Ed 1981;19:909–20.
[5] Larrondo L, Manley RSJ. J Polym Sci Phys Ed 1981;19:921–32.
[6] Larrondo L, Manley RSJ. J Polym Sci Phys Ed 1981;19:933–40.
[7] Yao L, Hass TW, Guiseppi-Elie A, Bowlin GWL, Simpson DG, Wnek GE. Chem Mater 2003;15:1860–4.
[8] Zeng J. PhD Dissertation, University of Marburg, Marburg; 2003.
[9] Zeng J, Hou H, Wendorff JH, Greiner A. e-polymers; 2004, no. 078.
[10] Zeng J, Hou H, Wendorff JH, Greiner A. Macromol Rapid Commun 2005;26:1557–62.
[11] Dror Y, Salalha W, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Langmuir 2003;19:7012–20.
[12] Ko F, Gogotsi Y, Ali A, Naguib N, Ye H, Yang Guoliang L, et al. Adv Mater 2003;15:1161–5.
[13] Dror Y, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Langmuir 2004;20:9852–5.
[14] Lim J, Lee C, Kim S, Kim I, Kim S. J Macromol Sci Part A Pure Appl Chem 2006;43:785–96.
[15] Lim J-M, Moon J-H, Yi Gi-Ra, Heo Ch-J, Yang S-M. Langmuir 2006;22:3445–9.
[16] Li D, Xia Y. Nano Lett 2003;3:555–60.
[17] Watthanaarun J, Pavarajarn V, Supaphol P. Sci Technol Adv Mater 2005;6:240–5.
[18] Park S, Lee DY, Lee M-H, Lee S-J, Kim B-YJ. Korean Ceram Soc 2005;42:548–53.
[19] Nuansing W, Ninmuang S, Jarernboon W, Maensiri S, Seraphin S. Mater Sci Eng B 2006;131:147–55.
[20] Lee DY, Kim B-Y, Lee S-J, Lee M-H, Song Y-S, Lee J-YJ. Korean Phys Soc 2006;48:1686–90.
[21] Jing N, Wang M, Kameoka J. J Photopolym Sci Technol 2005;18:503–6.
[22] Azad A-M, Matthews T, Swary J. Mater Sci Eng B Solid State Mater B 2005;123:252–8.
[23] Azad A-M. Mater Lett 2006;60:67–72.
[24] Jin H-J, Fridrikh SV, Rutledge GC, Kaplan DL. Biomacromolecules 2002;3:1233–9.
[25] Wang M, Jin H-J, Kaplan DL, Rutledge GC. Macromolecules 2004;37:6856–64.
[26] Lee S-W, Belcher AM. Nano Lett 2004;4:387–90.
[27] Gensheimer M, Brandis-Heep M, Thauer R, Wendorff JH, Greiner A. Adv Mater, in press.
[28] Bognitzki M, Hou H, Ishaque M, Frese T, Hellwig M, Schwarte C, et al. Adv Mater 2000;12:637–40.
[29] Hohman MM, Shin M, Rutldge G, Brenner MP. Phys Fluids 2001;13:2201–20.
[30] Deitzel JM, Kleinmeyer J, Harris D, Tan NCB. Polymer 2001;42:261–72.