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Biologically Inspired Hierarchical Design of Nanocomposites Based on Poly(ethylene oxide) and Cellulose Nanofibers

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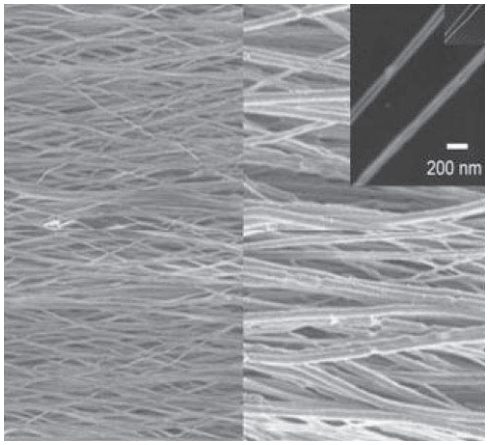
Attempts to create hierarchically structured, uniaxially oriented nanocomposites comprising cellulose nanowhiskers (CNWs), which promise anisotropic mechanical properties, are exceedingly rare. We report here the fabrication of uniaxially-oriented arrays of microfibers based on poly(ethylene oxide) (PEO) and CNWs by electrospinning. Compared with the neat PEO fibers, the incorporation of CNWs within the fibers increased the storage modulus (E') of arrays along the fiber axis of the PEO/CNW nanocomposite fibers. Successful incorporation of the CNWs within each of the as-spun PEO/CNW nanocomposite fibers in the direction parallel to the fiber axis was verified by both scanning and transmission electron microscopy.



Introduction

Cellulose is the most ubiquitous and abundant polymer in nature. The chemical configuration (Figure 1a) promotes crystallization into hydrogen-bonded, uniaxially-oriented primary structures, which are the origin of interesting properties such as high thermal stability, insolubility in water and intriguing mechanical properties.[1] The latter originate from the hierarchical design of native cellulosic materials: cellulose chains assemble into crystals to form microfibrils, which, together with other components, aggregate into larger macroscopic fibers. These hierarchical structures can be deconstructed by hydrolysis; if the process is carefully controlled, highly crystalline cellulose nanofibers, commonly referred to as "nanowhiskers" can be isolated from native cellulose. Typical sources include wood, tunicates, cotton, and others.[1] Cellulose nanowhiskers (CNWs) display a high aspect ratio (10–100), with diameters between 4 and 25 nm, depending on the source. Due to the high level of uniaxial orientation CNWs exhibit on-axis elastic moduli of 100–150 GPa.[2–4]

The idea to use CNWs to construct semi-artificial nanocomposites has received significant attention.[5–9] Favier et al. were the first to report a significant improvement of the mechanical properties of a poly[styrene-*co*-(butyl acrylate)] latex upon incorporating small amounts of CNWs isolated from tunicates.[10] In the meantime, a broad range of nanocomposites comprising CNWs has been

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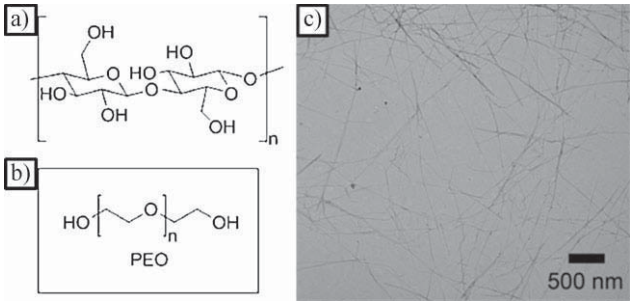

Figure 1. Chemical structure of a) CNWs, b) polyethylene oxide (PEO), and c) transmission electron microscopy (TEM) image of CNWs isolated from tunicates.

studied.[11–23] In isotropic nanocomposites the CNWs, if well dispersed and used in a concentration above the percolation limit, form a percolating network.[24] Stress transfer is facilitated by hydrogen-bonding between the surface hydroxyl groups[25] and the mechanical properties are well described by a percolation model.[26,27,10] Below the percolation limit the reinforcement is less pronounced and can be described by the Halpin–Kardos model.[1]

Attempts to create hierarchically-structured, uniaxially-oriented nanocomposites comprising CNWs, which promise anisotropic mechanical properties, are rare. It has been reported that in neat whisker suspensions (without polymer) orientation can be induced by a shearing force with the orientation occurring in the direction perpendicular to the shear direction for low shear rates and along the shear direction for higher rates.[28] Strong magnetic[29–33] and electric[34] fields were also used to orient nanowhisker suspensions. We report here the fabrication of uniaxially oriented arrays of microfibers based on poly(ethylene oxide) and CNWs by electrospinning. This method is ideal for the fabrication of thin fibers (μm to nm range) and has been used to orient a variety of fillers along the fiber axis, including single-walled[35,36] or multi-walled[37–39] carbon nanotubes, TiO_2 nanowires,[40] and bacterial cellulose.[41] Electrospinning can also induce anisotropy on the molecular scale, as polymer chains show preference for uniaxial alignment along the fiber axis.[42–47] Peresin et al. showed that fibrous nanocomposites of poly(vinyl alcohol) and CNWs isolated from ramie can be produced via electrospinning, although uniaxial alignment of the electrospun fibers was not pursued.[48] Kakade and coworkers showed that macroscopic alignment of polymer nanofibers, as well as PEO chains, parallel to the fiber axis, can be achieved by electrospinning in a field between two electrically-charged deposition plates.[46] This method was employed here to create uniaxially-oriented nanocomposite arrays based on PEO and CNWs isolated from tunicates, a nuisance marine species. For the first time, mechanical reinforcement of such hierarchically oriented materials is demonstrated.

Experimental Section

Materials and Solution Preparation

Poly(ethylene oxide) (PEO) ($\overline{M}_w \approx 3\,000\,000$ Da) was purchased from Polysciences (USA). CNW were isolated by sulfuric acid hydrolysis from tunicates (*Styela Clava*), using a previously reported procedure.[10,49,50] The nanowhiskers were dispersed in de-ionized water (6.3 mg · mL^{-1}) and sonicated before mixing with the polymer at different weight ratios (i.e., 100:0, 95:5, 90:10, and 85:15 polymer:CNW). The resulting mixtures were diluted with de-ionized water to adjust the overall concentrations to 2.5, 2.6, 2.8, and 2.9% w/v (i.e., to maintain a PEO concentration of ca. 2.5% w/v) and the mixtures were stirred for 1 d at room temperature before electrospinning.

Electrospinning

Electrospinning was carried out under fixed electrical potential (15 kV), collection distance (25 cm), and collection time (24 h) to produce uniaxially oriented, film-like arrays of the fibers. The final thickness of the fabric was in the range of 20–30 μm. Briefly, each mixture was placed in a 10 mL plastic syringe with a blunt 18-gauge stainless steel hypodermic needle being used as the nozzle. An aluminum frame (15.2 cm × 15.2 cm with three 2 cm × 10 cm openings) was used as collection plate that allowed for fiber alignment across the openings. A Gamma High-Voltage Research ES30P DC power supply (Florida, USA) was connected to the needle (+), while the ground electrode was connected to the collector plate. A feed rate of 0.5 mL · min^{-1} was maintained by an ALADDIN-100 syringe pump (World Precision Instruments, USA).

Morphology

The morphological appearance of the electrospun fibers was examined using a Nova nanoSEM 600 scanning electron microscope (SEM) from FEI Company (USA). The fiber diameters of electrospun samples were determined using SEM images at 5000× magnification; average values were determined from at least 100 measurements for each spinning condition. Electrospun PEO/CNW fibers, as well as neat CNWs, were examined using a JEOL 1200EX transmission electron microscope (TEM). Nanowhisker samples were prepared by deposition of 5 mL of the nanowhisker dispersion on carbon-coated copper grids. Electrospun PEO/CNW fibers were aligned across the opening of the aluminum frame for 1 min and then the copper grid was held by a pair of tweezers to take the aligned fiber out of the opening directly.

Mechanical Properties

The mechanical properties of rectangular electrospun PEO/CNW fiber arrays were investigated using dynamic mechanical thermal analysis (DMTA) measurements on a DMA Q800 V7.4 in tensile mode at an oscillation frequency of 1 Hz, a static force of 10 mN, oscillation amplitude of 15.0 μm and an automatic tension setting of 125%. The measurements were carried out over the temperature range of 20–50 °C at 3 °C · min^{-1}.

Results and Discussion

The CNWs used in this study were extracted from clubbed tunicates (Styela Clava), a marine nuisance species, according to previously-established protocols.[10,49,50] As can be seen from the TEM images shown in Figure 1c, these CNWs are characterized by an unusually high aspect ratio (i.e., 100 on average), with an average width of ca. 20 nm and an average length of ca. 2 μm.[10,49,50] Previous work by Favier et al.[10] and Weder coworkers[25] suggests that CNWs isolated from tunicates display a more pronounced reinforcing effect than other types of CNWs, perhaps on account of the higher aspect ratio. PEO, shown in Figure 1b, was used as the matrix in the present study, as it is easily processed into fibers by electrospinning and is readily soluble in water,[46] an excellent dispersant for the CNWs. Aqueous solutions containing PEO at a concentration of 2.5–2.9% w/v and 0–20% w/w nanowhiskers (relative to the PEO) served as dope for the electrospinning experiments. These were conducted using an electric field of 15 kV applied between the needle tip and an collection plate with slit-like openings. The slit-like openings allowed for fiber alignment across the opening gap.[46] This enabled the fabrication of uniaxially oriented arrays of PEO/CNW nanocomposites. The morphological characterization of these materials was carried out using both SEM and TEM, which revealed clearly the hierarchical organization of these systems. Figure 2 shows the SEM images of neat PEO fibers (Figure 2a) and PEO/CNW nanocomposite fibers (Figure 2b–d) of varying CNW content (i.e., 5, 10, and 15% w/w). Indeed, all of the electrospun fiber arrays were deposited in a uniaxially-aligned manner across the gap in the collection plate. The uniaxial alignment was maintained over the entire deposition period, but the SEM images show some imperfections in the alignment and the presence of voids; this is attributed to the surface charge repulsion of the fibers.[51,52] Detailed inspection of the SEM images of the fibers shows round cross-sectional diameters in the range of 430 to 460 nm (Table 1). Only a slight difference in the appearance of the neat PEO and the PEO/CNW nanocomposite fibers was observed. In both cases, the fiber surface is very smooth. The average fiber diameter slightly decreased with increasing CNW content, which is attributed to the slight increase in the overall concentration and the increased viscosity upon the addition of CNWs to the spinning mixtures. These results are consistent with previously published studies, which reported decreased

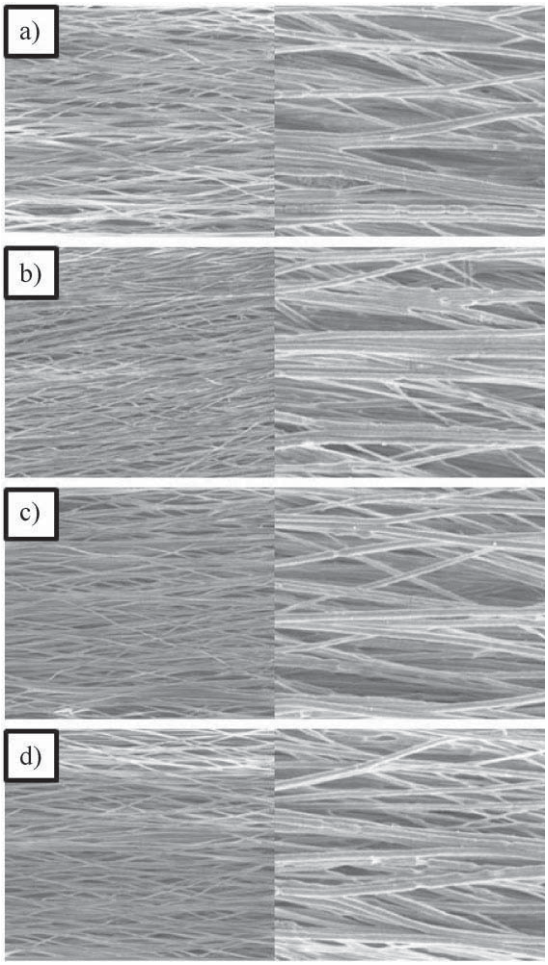

Figure 2. Scanning electron microscopy (SEM) images of the uniaxially oriented arrays of electrospun fibers of neat PEO (a) and PEO/CNW nanocomposites (b–d). b) 5% w/w CNW c) 10% w/w CNW d) 15% w/w CNW. Shown are images with a magnification of 5000× ($60 \times 60\ \mu m^2$, left) and 10 000× ($15 \times 15\ \mu m^2$, right).

Table 1. Composition of spinning solutions, average fiber diameters, and storage moduli (E') of the electrospun fiber arrays PEO/CNW.

PEO/CNW concentration [% w/v]	CNW content [% w/w]	Average fiber diameter [nm]	Storage modulus (E') of array [MPa]
2.5	0	459 ± 0.2	163 ± 14
2.6	5	454 ± 0.1	234 ± 96
2.8	10	448 ± 0.1	267 ± 25
2.9	15	437 ± 0.2	324 ± 10

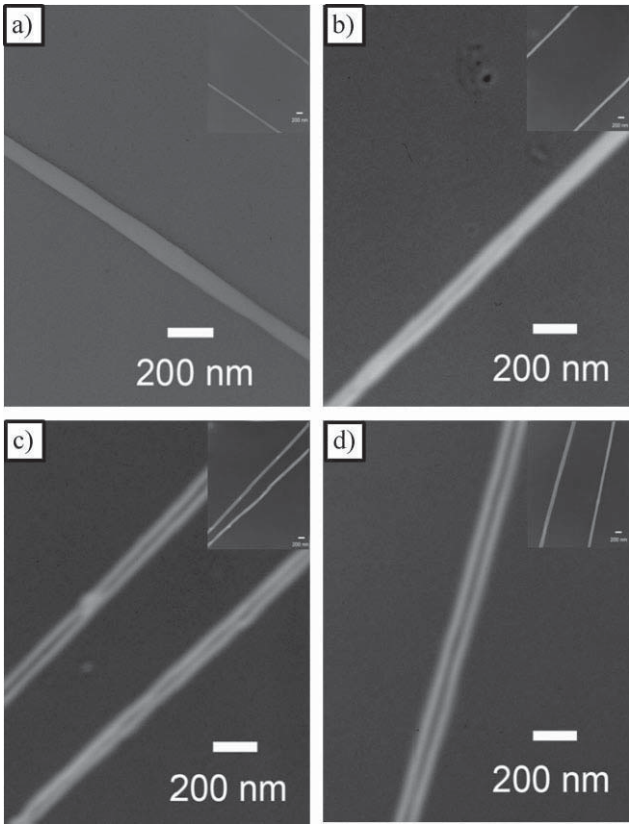

Figure 3. Transmission electron microscopy (TEM) images of individual electrospun fibers of neat PEO (a) and PEO/CNW nanocomposites (b–d), b) 5% w/w CNW, c) 10% w/w CNW, d) 15% w/w CNW.

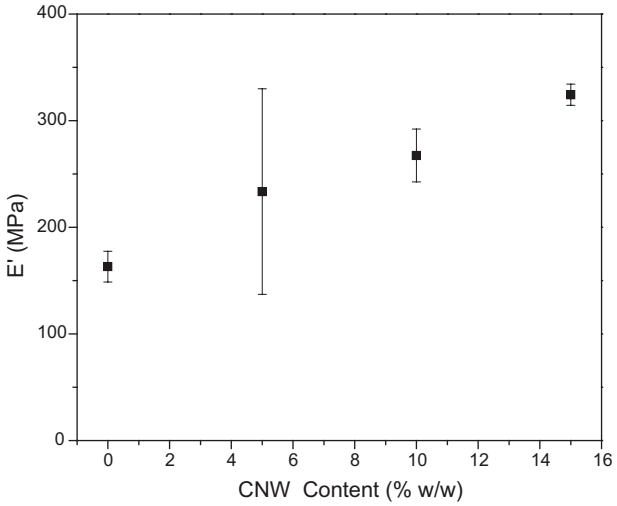

Figure 4. Storage modulus (E'), determined at room temperature, of arrays of electrospun fibers of neat PEO and PEO/CNW nanocomposites as function of CNW content.

fiber diameters when the viscosity of the spinning solution increased and the mass throughput of the spinning solution decreased.[53,54]

The incorporation of the CNWs into the electrospun fibers and, in particular, their alignment within the fibers was probed using TEM (Figure 3). Only fiber segments with diameters in the range of 90–110 nm were suitable for TEM observation. In view of the fact that the average length of the CNWs (i.e., ca. 2 μm) used is substantially greater than the diameter of the electrospun fibers (430–460 nm in Figure 2 and 90–110 nm in Figure 3), the absence of any protruding segments of CNWs from the PEO/CNW nanocomposite fibers, as revealed by both SEM and TEM images (Figure 2 and 3) suggests that the CNWs are incorporated well within the fibers in an oriented manner. Figure 3a shows the TEM image of an individual neat PEO fiber segment. The image does not show any specific features. On the contrary, darker areas can be seen in the TEM images of the PEO/CNW nanocomposite fibers, which correspond to the width of the whiskers (ca. 20 nm) and are much smaller than the fiber diameter (ca. 90–110 nm). The images suggest that the CNWs reside at the core of the fibers and are embedded within the fibers in the direction parallel to the fiber axis, with a high level of uniaxial alignment. Thus the observations in the SEM and TEM images suggest the targeted hierarchical structure, that is cellulose molecules being first assembled into highly anisotropic whiskers, which are embedded within the electrospun fibers in a uniaxially-oriented manner, which, in turn, are assembled into uniaxially-oriented arrays. This hierarchical architecture is the result of electrostatic interactions and shear forces of the process.[46,51,52] According to previously-published reports, the PEO chains are expected to orient along the fibers axis,[46] but this was not investigated in the present study.

To study the mechanical properties of the fiber arrays of PEO and PEO/CNW nanocomposites, rectangular sections of the arrays were cut away from the aligned fibers across the gap of the collection plate. The mechanical properties of these samples were explored by DMTA. The storage moduli (E') of the neat PEO and the PEO/CNW nanocomposite fiber arrays, measured at 25 °C, are compiled in Table 1 and Figure 4. Based on the obtained results, the reinforcement effect resulting from the presence of the CNWs is clearly evident. Specifically, E' doubled from ca. 163 MPa for the neat PEO fiber arrays to ca. 324 MPa for the nanocomposite fiber arrays comprising 15% w/w of the CNWs. The observed reinforcements is lower than expected based on percolation and Halpin–Kardos models, but it should be noted that the mechanical properties of the uniaxial arrays are, to a large extent, governed by the fact that the electrospun films are largely "disconnected" in the transverse direction. We surmise that significant improvements could be made by the use of an additional binder or post-processing scheme that reduce void space and merge films together.

Conclusion

Poly(ethylene oxide)/cellulose nanowhisker nanocomposite fibers with average diameters of 437–459 nm were prepared by electrospinning. For the first time, macroscopic uniaxial alignment of such electrospun, cellulose-containing fibers was pursued by deposition on a collection plate with gap. Electron microscopy studies revealed high levels of uniaxial orientation at different levels, i.e. of the nanowhiskers within the PEO fibers and of the PEO fibers with respect to another. DMTA data show that the storage moduli E' of arrays of aligned electrospun PEO/CNW nanocomposite fibers are 1.5–2 times greater than those of the neat PEO counterparts. While all ideas employed herein have individually been used, they were, to our best knowledge, combined for the first time to create hierarchically structured, uniaxially oriented arrays of thin polymer fibers containing cellulose-nanowhiskers with improved mechanical properties.

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Keywords: cellulose; electrospinning; fibers; hierarchical structure; nanocomposite; nanowhiskers

[1] S. J. Eichhorn, A. Dufresne, M. Aranguren, N. E. Marcovich, J. R. Capadona, S. J. Rowan, C. Weder, W. Thielemans, M. Roman, S. Renneckar, W. Gindl, S. Veigel, J. Keckes, H. Yano, K. Abe, M. Nogi, A. N. Nakagaito, A. Mangalam, J. Simonsen, A. S. Benight, A. Bismarck, L. A. Berglund, T. Peijs, *J. Mater. Sci.* **2010**, *45*, 1.
[2] I. Sakurada, Y. Nukushina, T. Ito, *J. Polym. Sci.* **1962**, *57*, 651.
[3] K. Tashiro, M. Kobayashi, *Polymer* **1991**, *32*, 1516.
[4] S. J. Eichhorn, G. R. Davies, *Cellulose* **2006**, *13*, 291.
[5] A. Dufresne, *Compos. Interfaces* **2000**, *7*, 53.
[6] N. L. Garcia de Rodriguez, W. Thielemans, A. Dufresne, *Cellulose* **2006**, *13*, 261.
[7] M. Samir, F. Alloin, A. Dufresne, *Biomacromolecules* **2005**, *6*, 612.
[8] M. Samir, F. Alloin, J. Y. Sanchez, A. Dufresne, *Polymer* **2004**, *45*, 4149.
[9] A. Sturcova, G. R. Davies, S. J. Eichhorn, *Biomacromolecules* **2005**, *6*, 1055.
[10] V. Favier, H. Chanzy, J. Y. Cavaille, *Macromolecules* **1995**, *28*, 6365.
[11] M. Samir, F. Alloin, J. Y. Sanchez, N. El Kissi, A. Dufresne, *Macromolecules* **2004**, *37*, 1386.
[12] L. Chazeau, J. Y. Cavaille, G. Canova, R. Dendievel, B. Boutherin, *J. Appl. Polym. Sci.* **1999**, *71*, 1797.
[13] D. Dubief, E. Samain, A. Dufresne, *Macromolecules* **1999**, *32*, 5765.
[14] M. N. Angles, A. Dufresne, *Macromolecules* **2000**, *33*, 8344.
[15] N. Ljungberg, C. Bonini, F. Bortolussi, C. Boisson, L. Heux, J. Y. Cavaille, *Biomacromolecules* **2005**, *6*, 2732.
[16] A. Morin, A. Dufresne, *Macromolecules* **2002**, *35*, 2190.
[17] K. Shanmuganathan, J. R. Capadona, S. J. Rowan, C. Weder, *Prog. Polym. Sci.* **2010**, *35*, 212.
[18] J. R. Capadona, K. Shanmuganathan, S. Triftschuh, S. Seidel, S. J. Rowan, C. Weder, *Biomacromolecules* **2009**, *10*, 712.
[19] J. R. Capadona, O. Van Den Berg, L. A. Capadona, M. Schroeter, S. J. Rowan, D. J. Tyler, C. Weder, *Nat. Nanotechnol.* **2007**, *2*, 765.
[20] K. Shanmuganathan, J. R. Capadona, S. J. Rowan, C. Weder, *J. Mater. Chem.* **2010**, *20*, 180.
[21] K. Shanmuganathan, J. R. Capadona, S. J. Rowan, C. Weder, *Acs Appl. Mater. Interfaces* **2010**, *2*, 165.
[22] Q. J. Wu, M. Henriksson, X. Liu, L. A. Berglund, *Biomacromolecules* **2007**, *8*, 3687.
[23] X. D. Cao, H. Dong, C. M. Li, *Biomacromolecules* **2007**, *8*, 899.
[24] O. van den Berg, M. Schroeter, J. R. Capadona, C. Weder, *J. Mater. Chem.* **2007**, *17*, 2746.
[25] J. R. Capadona, K. Shanmuganathan, D. J. Tyler, S. J. Rowan, C. Weder, *Science* **2008**, *319*, 1370.
[26] M. Takayanagi, S. Minami, S. Uemura, *J. Polym. Sci. Part C-Polym. Symp.* **1964**, *5*, 113.
[27] N. Ouali, J. Y. Cavaille, J. Perez, *Plast. Rubber Compos. Process. Appl.* **1991**, *16*, 55.
[28] N. Yoshiharu, K. Shigenori, W. Masahisa, O. Takeshi, *Macromolecules* **1997**, *30*, 6395.
[29] E. D. Cranston, D. G. Gray, *Sci. Technol. Adv. Mater.* **2006**, *7*, 319.
[30] F. Kimura, T. Kimura, *Sci. Technol. Adv. Mater.* **2008**, *9*, 1.
[31] F. Kimura, T. Kimura, M. Tamura, A. Hirai, M. Ikuno, F. Horii, *Langmuir* **2005**, *21*, 2034.
[32] I. Kvien, K. Oksman, *Appl. Phys. a-Mater. Sci. Process.* **2007**, *87*, 641.
[33] J. Sugiyama, H. Chanzy, G. Maret, *Macromolecules* **1992**, *25*, 4232.
[34] D. Bordel, J. L. Putaux, L. Heux, *Langmuir* **2006**, *22*, 4899.
[35] J. B. Gao, A. P. Yu, M. E. Itkis, E. Bekyarova, B. Zhao, S. Niyogi, R. C. Haddon, *J. Am. Chem. Soc.* **2004**, *126*, 16698.
[36] W. Salalha, Y. Dror, R. L. Khalfin, Y. Cohen, A. L. Yarin, E. Zussman, *Langmuir* **2004**, *20*, 9852.
[37] Y. Dror, W. Salalha, R. L. Khalfin, Y. Cohen, A. L. Yarin, E. Zussman, *Langmuir* **2003**, *19*, 7012.
[38] J. J. Ge, H. Q. Hou, Q. Li, M. J. Graham, A. Greiner, D. H. Reneker, F. W. Harris, S. Z. D. Cheng, *J. Am. Chem. Soc.* **2004**, *126*, 15754.
[39] M. V. Jose, B. W. Steinert, V. Thomas, D. R. Dean, M. A. Abdalla, G. Price, G. M. Janowski, *Polymer* **2007**, *48*, 1096.
[40] H. S. Shim, S. I. Na, S. H. Nam, H. J. Ahn, H. J. Kim, D. Y. Kim, W. B. Kim, *Appl. Phys. Lett.* **2008**, *92*, 183107.

[41] W. I. Park, M. Kang, H. S. Kim, H. J. Jin, *Macromol. Symp.* **2007**, *249*, 289.
[42] S. F. Fennessey, R. J. Farris, *Polymer* **2004**, *45*, 4217.
[43] W. A. Yee, M. Kotaki, Y. Liu, X. H. Lu, *Polymer* **2007**, *48*, 512.
[44] A. Bianco, G. Iardino, A. Manuelli, C. Bertarelli, G. Zerbi, *Chemphyschem* **2007**, *8*, 510.
[45] L. M. Bellan, H. G. Craighead, *Polymer* **2008**, *49*, 3125.
[46] M. V. Kakade, S. Givens, K. Gardner, K. H. Lee, D. B. Chase, J. F. Rabolt, *J. Am. Chem. Soc.* **2007**, *129*, 2777.
[47] Y. Liu, C. Pellerin, *Macromolecules* **2006**, *39*, 8886.
[48] M. S. Peresin, Y. Habibi, J. O. Zoppe, J. J. Pawlak, O. J. Rojas, *Biomacromolecules* **2010**, *11*, 674.
[49] V. Favier, G. R. Canova, S. C. Shrivastava, J. Y. Cavaille, *Polym. Eng. Sci.* **1997**, *37*, 1732.
[50] O. van den Berg, J. R. Capadona, C. Weder, *Biomacromolecules* **2007**, *8*, 1353.
[51] P. Katta, M. Alessandro, R. D. Ramsier, G. G. Chase, *Nano Lett.* **2004**, *4*, 2215.
[52] D. Li, Y. L. Wang, Y. N. Xia, *Nano Lett.* **2003**, *3*, 1167.
[53] T. Jarusuwannapoom, W. Hongroijanawiwat, S. Jitjaicham, L. Wannatong, M. Nithitanakul, C. Pattamaprom, P. Koombhongse, R. Rangkupan, P. Supaphol, *Eur. Polym. J.* **2005**, *41*, 409.
[54] C. J. Thompson, G. G. Chase, A. L. Yarin, D. H. Reneker, *Polymer* **2007**, *48*, 6913.