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Polydiacetylene Supramolecules in Electrospun Microfibers: Fabrication, Micropatterning, and Sensor Applications**

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The generation of functional supramolecular structures through the self-assembly of small molecules continues to be a significant scientific endeavour.^[1] Molecularly assembled monomers that contain polymerizable units often serve as precursors to unique supramolecular structures that have meritorious features, for example, enhanced stability and chromogenic functions. In this regard, polydiacetylene (PDA) supramolecules, readily prepared by UV or γ irradiation of molecularly assembled diacetylene (DA) monomers, are attractive substances.^[2,3] The polymer backbone of PDAs consists of alternating alkene–alkyne structures. Owing to their intriguing stress-induced chromic transition (blue to red) and nonlinear optical properties, PDAs have been extensively investigated as potential chemosensors and photonic materials.^[4]

Recently, the embedment of PDA supramolecules in matrices and host molecules has been used advantageously for the creation of well-defined nano- and microscale structures and substances with unique optical, electronic, and mechanical properties. Several examples include helical tubular inorganic architectures that are prepared by using a chiral diacetylene monomer as a template molecule,^[5] PDA-silica nanocomposites that possess hexagonal, cubic, and lamellar structures,^[6] and hybrid sol-gel matrices with encapsulated antibody-containing PDAs for biosensor applications.^[7] The encapsulation of PDA supramolecules in polymer nano- or microfibers has not yet been reported.

Electrospinning has proven to be an efficient method for the formation of long polymer fibers with diameters in the range of nanometers to several micrometers.^[8] In this technique a high voltage is applied to a conductive capillary, which is attached to a reservoir containing a polymer solution. A charged polymer jet is ejected from the surface of the polymer

solution when the charge imbalance exceeds the surface tension of the polymer solution. Polymer fibers are formed when the jet stream, driven by electrostatic forces, moves to the grounded screen collector. Its characteristic merits allow the electrospinning technique to be uniquely applied to the rapid, cost-effective fabrication of PDA conjugated polymers in the form of microfibers with a large surface area. In this Communication we describe a simple but elegant approach for the generation of polymer microfibers containing embedded PDA supramolecules, based on the electrospinning technique.

The strategy employed in this study, schematically presented in Figure 1, initially involves DA monomers that are randomly distributed in an organic solvent before electrospinning. As the solvent evaporates during fiber formation, self-assembly of DA monomers takes place because the attractive forces between the DA monomers are larger than those between the DA monomers and matrix polymers. Polymerization of the self-assembled DA monomers should result in the formation of PDAs embedded within the polymer fibers. 10,12-Pentacosadiynoic acid (PCDA, $\text{CH}_3(\text{CH}_2)_{11}\text{C}\equiv\text{C}-\text{C}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$), a frequently employed DA monomer in

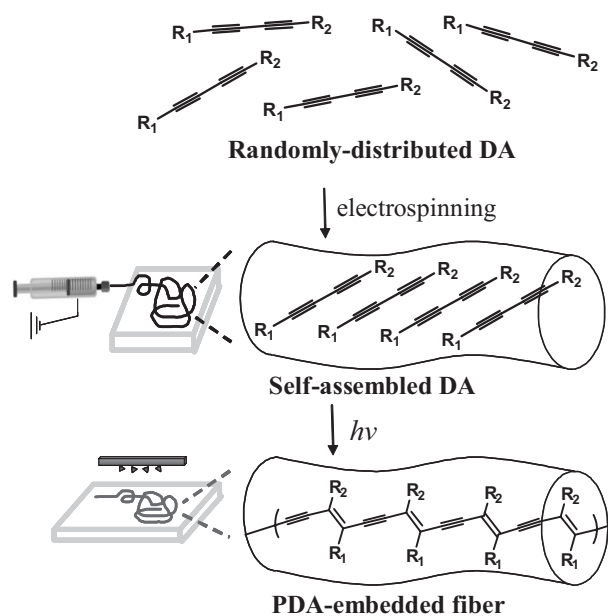


Figure 1. Schematic representation of the preparation of polymer microfibers-embedded with PDA supramolecules by using the electrospinning technique, followed by irradiation with UV light (254 nm).

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PDA chemistry, was used to test the proposed method. Poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) were selected as representative matrix polymers. Although our current investigations focused on PCDA, PDAs from other diacetylenes can be also created in polymer fibers (see the Supporting Information for more details).

Scanning electron microscopy (SEM) images of the electrospun fibers obtained from a chloroform solution containing PEO (weight-average molecular weight (M_w) 300 000 g mol^{-1} , 5 wt %) and PCDA (1.7 wt %) are displayed in Figure 2A and B. The SEM images show that the formed fibers have highly uniform diameters of ca. 3 μm . An optical microscopy

image of an electrospun fiber is shown in Figure 2C. To investigate if PCDA monomers self-assembled during fiber formation, the electrospun fiber shown in Figure 2C were irradiated with 254 nm UV light (1 mW cm^{-2}) for 3 min. Upon irradiation, the fiber developed a blue color when observed under an optical microscope (Fig. 2D), suggesting that PDAs were produced from PCDA monomers. The formation of PDA was further demonstrated by a color transition (blue to red) upon heating the blue-colored fiber at 100°C for 1 min (Fig. 2E). In agreement with the fact that PDAs fluoresce in the “red phase”, the heat-treated fiber exhibited strong fluorescence under a fluorescence microscope (Fig. 2F).

These results clearly support the conclusion that PDAs are generated in the electrospun fibers.

Beaded nanofibers were obtained when electrospinning was carried out on an acetone solution of PMMA (13 wt %) and PCDA (3.6 wt %). SEM images show that the fibers generated in this manner have diameters of 100–200 nm with beads of 3–4 μm (Fig. 2G). Under a fluorescence microscope, beaded nanofibers that were irradiated (254 nm, 1 mW cm^{-2} , 1 min) and then heat-treated (100°C , 3 min) fluoresced from microdot regions (Fig. 2H). Importantly, the fluorescent dots are linked along the direction of the fibers, yielding a 1D arrangement of PDA microbeads.

Interestingly, the generation of patterned color and fluorescent images with a single fiber was also possible by using a photolithographic technique (Fig. 3A and B). For example, photomasked UV irradiation (254 nm , 1 mW cm^{-2} , 3 min) of a single PMMA fiber encapsulated with PCDA resulted in patterned blue-color images (Fig. 3, left). Heating this patterned fiber at 110°C for 1 min generated patterned red-color optical (Fig. 3, middle) and fluorescence (Fig. 3, right) microscopy images.

Evidence for the formation of PDA supramolecules in electrospun polymer fibers derived from PCDA was obtained from Raman spectroscopy measurements. The Raman spectrum of a chloroform solution of monomeric PCDA, in which the acetylenic stretching band appears at 2257 cm^{-1} , is displayed in Figure 4A. When electrospun PCDA-embedded PEO fibers were irradiated with UV light for 3 min, the acetylenic stretching band of PCDA disappeared (Fig. 4B) and new bands, associated with conjugated alkene–alkyne structures, appeared at $2080 \text{ (C}\equiv\text{C)}$ and 1450 (C=C) . The band at 2080 cm^{-1} is characteristic of “blue-phase” PDAs.^[9]

To gain information about the nature of the PDA supramolecules in the electrospun microfibers, PEO fibers, obtained by the method described in Figure 2F, were placed on a slideglass, and washed with water to remove water-soluble PEO. SEM analysis of the water-treated polymer

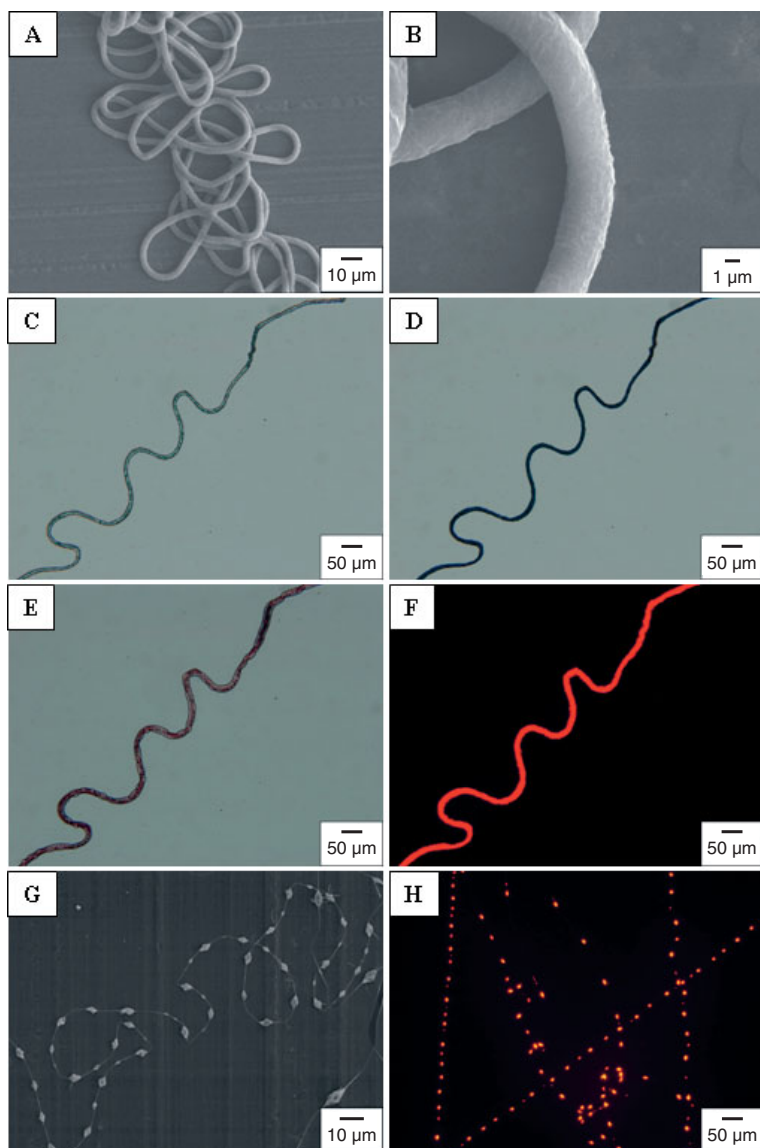


Figure 2. A,B) Scanning electron microscopy (SEM) images of PCDA-embedded PEO (chloroform, 5 wt %) fibers. C,D) Optical microscopy images of the fiber before and after 254 nm UV irradiation (1 mW cm^{-2} , 3 min), respectively. E,F) Optical and fluorescence microscopy images, respectively, obtained after heat treatment (100°C , 1 min) of the blue-colored fiber shown in Figure 2D. G,H) SEM and fluorescence images, respectively, of PCDA-embedded PMMA (acetone, 13 wt %) fibers.

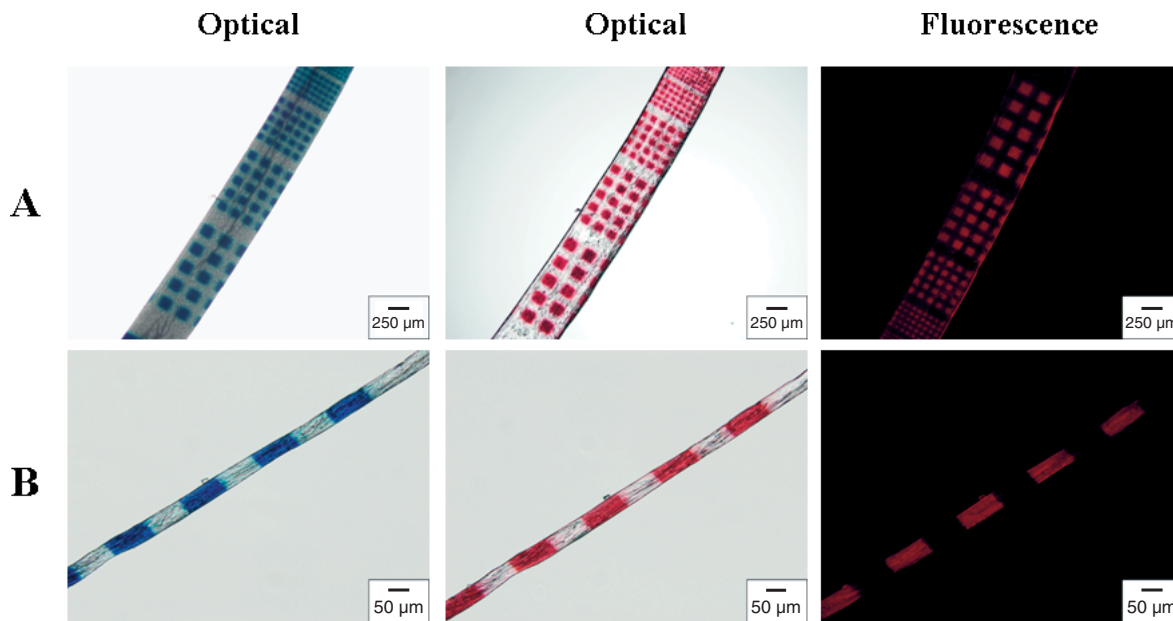


Figure 3. Patterned images of a single PCDA-embedded PMMA fiber, obtained by electrospinning of a CH_2Cl_2 solution containing (A) 30 and (B) 20 wt% PMMA (M_w : 120 000 g mol^{-1}). Optical images (left) obtained after UV irradiation of the electrospun fiber (254 nm, 1 mW cm^{-2} , 3 min). Optical (middle) and fluorescence (right) microscopy images obtained after heat treatment of the blue-patterned fiber (110°C , 1 min).

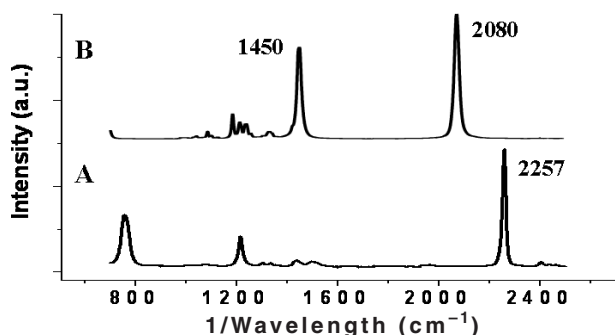


Figure 4. Raman spectra of (A) PCDA in chloroform and (B) PCDA-embedded PEO fibers after exposure to UV light (3 min).

fibers revealed that the PDA supramolecules exist as a distribution of amorphous PDA aggregates (see Supporting Information). The effect of the feed ratio between the diacetylene

monomer and matrix polymer on PDA formation in electrospun fibers was also investigated. In general, facile formation of PDA-embedded microfibers was observed at various DA/matrix ratios (1:9, 1:7, 1:5, or 1:3 wt %), unless when an excessive amount of DA monomer was used ($> 1:1$).

The final phase of the current investigation focused on the application of PDA-embedded polymer fibers as chemosensors. For this purpose, porous microfibers embedded with PDAs were prepared by electrospinning a CH_2Cl_2 solution containing PMMA (20 wt %) and PCDA (4 wt %), followed by UV irradiation (Fig. 5A and B). It is well-known that electrospinning with a solvent with a low boiling point, such as CH_2Cl_2 , yields highly porous polymer fibers.^[8b] Incubation of the porous PMMA microfibers, containing embedded polymerized PCDA, in an α -cyclodextrin (α -CD) solution (10 mM) resulted in the generation of red fluorescence (Fig. 5C). Much weaker fluorescence signals arose from fibers treated with β - and γ -CD (see Supporting Information). The promotion of

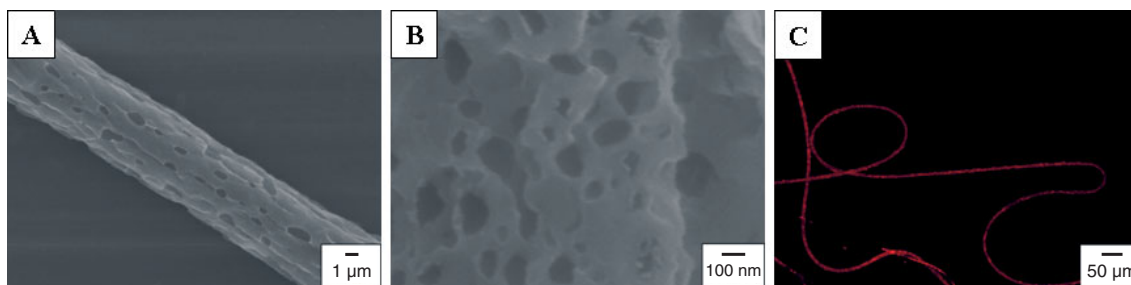


Figure 5. A,B) Scanning electron microscopy images of an electrospun PCDA-embedded PMMA fiber after photopolymerization. C) Fluorescence microscopy image of the polymer fiber after treatment with a 10 mM α -cyclodextrin solution (30°C , 30 min).

chromic transitions and fluorescence generation of PCDA-derived PDAs by α -CD and not by β - and γ -CD has been previously reported by our group.^[3b,c]

In conclusion, the work described herein has led to the development of a new approach for constructing PDA supramolecules in electrospun microfibers. Diacetylene monomers were found to self-assemble during fiber formation and afford PDAs upon photopolymerization. Patterned color and fluorescence images from a single electrospun fiber were also observed. In addition, the feasibility of PDA-embedded electrospun microfibers as potential sensor materials was demonstrated by fluorescence generation upon specific ligand-receptor interactions. This simple procedure for producing PDA-encapsulated polymer fibers should lead the way to the discovery of new and interesting PDA-based materials.

Experimental

Materials and Instruments: 10,12-Pentacosadiynoic acid (PCDA) and 10,12-docosadiynoic acid (DCDDA) were purchased from GFS Chemicals. PEO (with $M_w = 300\,000\text{ g mol}^{-1}$ and $M_w = 1\,000\,000\text{ g mol}^{-1}$; see Supporting Information) and PMMA ($M_w = 120\,000\text{ g mol}^{-1}$) were purchased from Aldrich. *N*-(2-(2-(2-Aminoethoxy)ethoxy) ethyl)pentacosyl-10,12-diyndiamide (PCDA-EDEA) was prepared as described earlier [3b]. Dipropyldocosyl-10,12-diyndiamide (DCDDA-bis-PA) was synthesized by coupling an acid chloride form of 10,12-docosadiynoic acid with propylamine. DCDDA-bis-PA: mp 112 °C; ¹H NMR (300 MHz, deuterated dimethyl sulfoxide, δ): 0.86 (t, 6H), 1.27–1.50 (m, 28H), 2.06 (t, 4H), 2.30 (t, 4H), 3.01 (q, 4H), 7.76 (s, 2H); ¹³C NMR (75 MHz, deuterated chloroform, δ): 11.34, 19.13, 22.87, 25.76, 28.22, 28.69, 28.86, 29.23, 29.17, 35.85, 42.12, 65.23, 77.19, 173.08; IR (KBr) $\nu = 3300, 3090, 2960\text{--}2850, 1640, 1550, 1460\text{ cm}^{-1}$.

Raman scattering measurements were performed with a HOLO LAB Series 5000 Raman microscope at a laser excitation wavelength of 785 nm. Optical and fluorescence microscopy images were obtained by using an Olympus BX51 W/DP70 microscope.

Electrospinning and Photopolymerization: A chloroform solution containing 167 mg (1.7 wt %) PCDA and 500 mg (5 wt %) PEO was prepared for electrospinning. The PCDA-containing PEO solution was pumped through a capillary connected with a metal syringe needle at a constant rate of 0.2 mL h⁻¹ by a syringe pump (KD Scientific, Model 200). The application of a high voltage (20 kV) to the metal syringe needle enabled the generation of microfibers, which were collected on the surface of a grounded aluminum plate (distance from the tip of the syringe to the plate: 18 cm). The collected fibers were kept in the dark. Photopolymerization was carried out by irradiation with 254 nm UV light (1 mW cm⁻²) to the electrospun polymer fiber embedded with PCDA for 3 min.

Scanning Electron Microscopy: SEM images of diacetylene supramolecules fiber were obtained on a JEOL JSM-6330F FE-SEM. The fibers collected on an aluminum foil were irradiated with 254 nm UV-light (1 mW cm⁻²) for 3 min, and then kept in vacuo for at least 12 h, followed by coating with Pt for 5 min. SEM images were obtained at an accelerating voltage of 10 or 15 kV.

Patterned Color and Fluorescence Images: The electrospun PCDA-embedded PMMA fiber was irradiated with 254 nm UV light (1 mW cm⁻²) for 3 min through a photomask, inducing the photopolymerization of diacetylene monomers only in the exposed areas. Blue-

colored patterned images were observed under an optical microscope. The fiber was then heated at 100 °C for 1 min to induce the blue-to-red color shift of the polydiacetylenes. The heat-treated fiber shows patterned fluorescence image under a fluorescence microscope (Olympus BX51 W/DP70).

Interaction of PDA-Embedded Fiber with Cyclodextrins: The PCDA-embedded PMMA (CH₂Cl₂, 20 wt %) fiber obtained was incubated in aqueous α -, β -, or γ -cyclodextrin (CD) solution (10 mM each) at 30 °C for 30 min. The fluorescence images were monitored under a fluorescence microscope.

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- [1] a) L. A. Estroff, A. D. Hamilton, *Chem. Rev.* **2004**, *104*, 1201. b) T. Shimizu, M. Masuda, H. Minamikawa, *Chem. Rev.* **2005**, *105*, 1401.
- [2] a) J. Song, J. S. Cisar, C. R. Bertozzi, *J. Am. Chem. Soc.* **2004**, *126*, 8459. b) B. N. Thomas, C. M. Lindemann, R. C. Corcoran, C. L. Contant, J. E. Kirsch, P. J. Persichini, *J. Am. Chem. Soc.* **2002**, *124*, 1227. c) G. Wang, R. I. Hollingsworth, *Adv. Mater.* **2000**, *12*, 871. d) Z. Yuan, C.-W. Lee, S.-H. Lee, *Angew. Chem. Int. Ed.* **2004**, *43*, 4197. e) R. W. Carpick, T. M. Mayer, D. Y. Sasaki, A. R. Burns, *Langmuir* **2000**, *16*, 4639. f) H. Bader, H. J. Ringsdorf, *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 1623. g) D. A. Frankel, D. F. O'Brien, *J. Am. Chem. Soc.* **1994**, *116*, 10057. h) Q. Huo, K. C. Russell, R. M. Leblanc, *Langmuir* **1999**, *15*, 3972. i) G. Wegner, *Makromol. Chem.* **1972**, *154*, 35. j) T. Kim, K. C. Chan, R. M. Crooks, *J. Am. Chem. Soc.* **1997**, *119*, 189.
- [3] a) J.-M. Kim, J.-S. Lee, H. Choi, D. Sohn, D. J. Ahn, *Macromolecules* **2005**, *38*, 9366. b) J.-M. Kim, Y. B. Lee, D. H. Yang, J.-S. Lee, G. S. Lee, D. J. Ahn, *J. Am. Chem. Soc.* **2005**, *127*, 17580. c) J.-M. Kim, J.-S. Lee, J.-S. Lee, S.-Y. Woo, D. J. Ahn, *Macromol. Chem. Phys.* **2005**, *206*, 2299.
- [4] a) S. Kolusheva, O. Molt, M. Herm, T. Schrader, R. Jelinek, *J. Am. Chem. Soc.* **2005**, *127*, 10000. b) G. Ma, A. M. Müller, C. J. Bardeen, Q. Cheng, *Adv. Mater.* **2006**, *18*, 55. c) C. Wang, Z. Ma, *Anal. Bioanal. Chem.* **2005**, *382*, 1708. d) D. H. Charych, J. O. Nagy, W. Spevak, M. D. Bednarski, *Science* **1993**, *261*, 585. e) A. Sarkar, S. Okada, H. Nakanishi, H. Matsuda, *Macromolecules* **1998**, *31*, 9174.
- [5] A. M. Seddon, H. M. Patel, S. L. Burkett, S. Mann, *Angew. Chem. Int. Ed.* **2002**, *41*, 2988.
- [6] Y. Yang, Y. Lu, M. Lu, J. Huang, R. Haddad, G. Xomeritakis, N. Liu, A. P. Malanoski, D. Sturmayer, H. Fan, D. Y. Sasaki, R. A. Assink, J. A. Shelnett, F. V. Swol, G. P. Lopez, A. R. Burns, C. J. Brinker, *J. Am. Chem. Soc.* **2003**, *125*, 1269.
- [7] I. Gill, A. Ballesteros, *Angew. Chem. Int. Ed.* **2003**, *42*, 3264.
- [8] a) Y. Dzenis, *Science* **2004**, *304*, 1917. b) R. Dersch, M. Steinhart, U. Boudriot, A. Greiner, J. H. Wendorff, *Polym. Adv. Technol.* **2005**, *16*, 276. c) D. Li, Y. Xia, *Adv. Mater.* **2004**, *16*, 1151. d) X. Wang, Y.-G. Kim, C. Drew, B.-C. Ku, J. Kumar, L. A. Samuelson, *Nano Lett.* **2004**, *4*, 331. e) D. H. Reneker, I. Chun, *Nanotechnology* **1996**, *7*, 216. f) P. Gupta, S. R. Trenor, T. E. Long, G. L. Wilkes, *Macromolecules* **2004**, *37*, 9211. g) Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, A. Greiner, *Adv. Mater.* **2003**, *15*, 1929. h) S. Megelski, J. S. Stephens, D. B. Chase, J. F. Rabolt, *Macromolecules* **2002**, *35*, 8456. i) J.-M. Lim, J. H. Moon, G.-R. Yi, C.-J. Heo, S.-M. Yang, *Langmuir* **2006**, *22*, 3445.
- [9] E. Giorgetti, M. Muniz-Miranda, G. Margheri, A. Giusti, S. Sottini, M. Alloisio, C. Cuniberti, G. Dellepiane, *Langmuir* **2006**, *22*, 1129.