Published in final edited form as:

Adv Opt Mater. 2016 March ; 4(3): 371–377. doi:10.1002/adom.201500552.

Active Polymer Microfiber with Controlled Polarization Sensitivity

Hongyan Xia¹, Ruxue Wang², Yingying Liu¹, Junjie Cheng¹, Gang Zou^{1,*}, Qijin Zhang¹, Douguo Zhang^{2,*}, Pei Wang², Hai Ming², Ramachandram Badugu³, and Joseph R. Lakowicz³

¹CAS Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, iChEM, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

²Department of Optics and Optical Engineering, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

³Center for Fluorescence Spectroscopy, Department of Biochemistry and Molecular Biology, University of Maryland School of Medicine, Baltimore, MD 21201, United States

Abstract

Controlled Polarization Sensitivity of an active polymer microfiber has been proposed and realized with the electrospun method. The fluorescence intensity guiding through this active polymer microfiber shows high sensitivity to the polarization state of the excitation light. What is more, the fluorescence out-coupled from tip of the microfiber can be of designed polarization state. Principle of these phenomena lies on the ordered and controlled orientation of the polydiacetylene (PDA) main chains inside polymer microfiber.

Keywords

active polymer microfiber; polarization; fluorescence; electrospun

Correspondence and requests for materials should be addressed to: Gang Zou, and D.G. Zhang. (gangzou@ustc.edu.cn, dgzhang@ustc.edu.cn).

*These authors contributed equally to this work.

Supporting Information

Supporting Information is available online from the Wiley Online Library or from the author.

Recently, one-dimensional (1D) micro-/nanostructures, such as silver-nanowires,^[1–3] semiconductor micro-nano wires,^[4–7] and polymer microfibers^[8,9] and so on, have been attracting great interest in designing integrated optoelectronic devices such as broadly tunable lasers,^[10] high-efficiency solar cells,^[11] optical waveguides,^[12] and photodetectors,^[13] because of their low dimensionality, tight optical confinement, and excellent waveguiding capabilities. Kim *et al*^[14] and Persano *et al*^[15] have made comprehensive reviews of the literatures on 1D micro-/nanostructures. As point out in these reviews, active polymer micro or nanofibers have the merits of low cost and versatile fabrication processes which exhibit an unequalled flexibility in terms of chemical composition, physical properties and achievable functionality. Due to these advantages, they have rapidly emerged as powerful tool for nanotechnologies and as building blocks of a wide range of devices. For examples, the teams of Pan, Tong and Duan had successfully fabricated 1D radial (core-shell) heterojunction structures^[16–18] made of inorganic materials (such as CdS and CdSe). Through tuning the composition of micro-nano wires, they realized the wavelength-tunable light emission (both incoherent and coherent emission), then developed the tunable nano-laser source, high gain submicrometer optical amplifier at near-infrared communication band.^[19] A. J. Das and V. D. Ta had reported microlasers based on polymer fibers which the fiber cross-sectional shape and dimension could be controlled.^[20, 21]

The sensitivity of the micro-/nanostructures to polarization of the excitation source, and the polarization property of the light emitted from the wires or fibers played important roles in optical components and have been investigated for a long time.^[22–27] However, there is few reports about controlled polarization sensitivity though controlling the order of molecular arrangement inside the microfibers. As we know, polarization is one of the basic parameters of electromagnetic waves, both for incoherent or coherent light source, which has great importance in laser source, optical circuit, optical imaging, and sensing devices and so on. To clearly dig out the polarization properties of the micro-/nanostructures, in our previous work, a 1D polymer microtube has been successfully fabricated through a hierarchical self-assembly method.^[28] The polarization of the out-coupled light was found to be independent on the propagation length, which was ascribed to the highly ordered molecular alignment of polymer main chains in the microtube. Whereas their polarization sensitivity are predetermined and cannot be modulated, limiting their practical applications.^[29,30] Accordingly, it remains challenging to develop novel 1D microstructures with controlled polarization sensitivity.

Herein, a novel method has been proposed to develop polymer microfiber with controlled polarization sensitivity or response. The 1D Polydiacetylene (PDA)-embedded microfibers were prepared by electrospinning^[31] and subsequent irradiation with a UV light source for photo-polymerization. Through tuning the polarization state the UV light, the order of the PDA main chains inside the microfiber can be precisely controlled, then its response to the polarization of the excitation source and the polarization states of the emitting fluorescence will be subsequently changed.

A schematic of the electrospinning process is shown in Figure 1a. Here we used a chloroform solution containing 5 wt% of 10,12-Pentacosadiynoic acid (PCDA) monomer

and 20 wt% of polystyrene (PS). The prepared microfibers have the average diameter of about 2 μm (Figure 1b and Figure S1a). Then upon irradiation of microfibers with unpolarized UV light linearly polarized or circularly polarized UV light (at 313 nm wavelength) for 10 min, PCDA monomers evolved into PDA polymers. The white microfibers became blue (Figure S1b) and upon heating to 80°C for 10 min, PDA-embedded electrospun microfibers showed reddish coloration (Figure S1c) and emitted red fluorescence (Figures S1d). The blue microfibers exhibited strong absorption bands at 585 and 645 nm, indicating the formation of PDA main chains (Figure S2a i), while the red microfibers exhibited strong absorption bands at 548 and 498 nm (Figures S2a ii). Figure S2b i and Figure S2b ii showed the fluorescence spectra of the PDA-embedded electrospun microfiber after photo-polymerized before and after heat-treatment at 80°C for 10 min. Fluorescence and time-resolved fluorescence characterizations confirmed that the existence of a PS matrix did not have a significant effect on the fluorescence properties of PDA.^[31] Confocal fluorescence imaging showed bright and uniform fluorescence intensity along the longitudinal axis of the PDA microfibers (Figure S1d). PDA assemblies formed highly ordered lamellar stacking structures with an intense (100) reflection at 4.6 nm was demonstrated by Small-angle X-Ray Diffraction (SXRD) analysis (as shown in Figure S3). The length of a fully extended monomer PCDA molecule is about 2.7 nm, thus each of the observed lamella structures contains bilayered units of PCDA molecules. And we envisioned the central regions of the bilayered units are being composed of carboxyl groups with hydrogen-bonding interactions and outer regions contain the alkyl side chains. No diffraction peaks for PS could be detected by SXRD of pure PS microfibers or the PDA-embedded microfibers, indicating that PS is in the amorphous phase within the microfibers. Figure 1b shows the scanning electron microscopy (SEM) characterization of the as-prepared PDA-embedded electrospun microfibers and cross-sectional SEM image of the broken microfiber which shows the diameter about 2 μm .

Firstly, a green laser beam of 532 nm wavelength was focused by an objective onto various spots along the microfiber which was polymerized with an unpolarized UV light. A notable fluorescence spot at the tip of the microfiber was observed, while comparatively weaker emission emanated from the body (except the two ends of the fiber). This phenomenon suggests that microfiber is fluorescent and the emitted fluorescence can be guided through the microfiber (Figure 1c). What is more, the fluorescence could even be guided along the bent PDA microfiber which functioned as a flexible waveguide (Figure S4). To assess the propagation losses in the microfiber, the excited spot is defined as point E1, the emission spot at tip of the fiber as point E2. The fluorescence images were captured while exciting at different positions of the microfiber (Figure 1c, point E1 is changed), then the fluorescence intensity from the tip (point E2, position is fixed) as a function of the distance L (μm , between point E1 and E2) can be derived, as shown in Figure 1d. A single exponential fit to the data yielded a propagation loss of $\alpha = 50 \text{ cm}^{-1}$ ($\pm 10\%$) for the loss coefficient, corresponding to the transmission loss of $0.022 \text{ dB } \mu\text{m}^{-1}$ (Figure 1d). Similar propagation losses ranging from 40 to 100 cm^{-1} were measured for other PDA microfibers fabricated with the same method, which is much lower than that of conjugated polymer fibers (ranging from 100 to 2000 cm^{-1}).^[32–36] The lower propagation losses should be ascribed to the preferential organization of monomer molecules induced by electrospinning and the

resulting preferential alignment of polymer main chains within the microfiber, which can reduce the self-absorption of the guided fluorescence signal.

Except for the low propagation losses, the prepared microfiber showed sensitivity to polarization of the excitation light. As shown in Figure S5, a polarizer and a half wave plate are placed after the excitation laser system to ensure constant beam intensity while the polarization orientation (α : as cross angle with respect to the long axis (X-axis) of the microfiber) laser beam is changed. By rotating the half wave plate, we recorded the fluorescence intensity from point E2 as a function of angle α (Figure 2a). The excitation wavelength was 532 nm. For the PDA microfiber irradiated with un-polarized UV light, the results show that the fluorescence intensity from point E2 is sensitive to the polarization direction (angle α , linear polarization) of the excitation beam. The maximum intensity occurred at $\alpha = 120^\circ$ or 300° (Figure 2b). Because the un-polarized light was adopted in the fabrication process, so this kind of polarization sensitivity can only be ascribed to the electrospun procedure. [37–40]

Secondly, we used linearly-polarized UV light of various orientations (θ defined as the polarization direction of the UV light with respect to long axis of the fiber) for the photopolymerization process. Figure 3a,b,c show that the change of fluorescence intensity from point is similar as that on Figure 2b. However, the maximum intensity occurred at different α in case of different θ . The phenomena means that the polarization sensitivity induced by the electrospun procedure can optically controlled by the UV light. Furthermore, if circularly-polarized UV light was employed for the polymerization process, the intensity from point E2 was found to be independent on the polarization of the excitation laser beam, meaning that their intrinsic anisotropy induced by the electrospun process was erased by the circular polarized UV light (Figure 3d). To the best of our knowledge, it is the first time that the elimination of the intrinsic polarization anisotropy in 1D conjugated polymer microfiber has been realized. The mechanism of this phenomenon can be attributed to the isotropic electric-field component of the circularly-polarized beam. The fluorescence with polarization isotropy is of great value in fluorescence based bio-imaging and sensing. The microfiber with these unique polarization properties also can be used for the rational design of novel polarization-related photonic devices.

The effect of angle α on the emitted fluorescence intensity (Figure 2 and Figure 3) can be ascribed to the highly ordered alignment of PDA main chains inside the microfiber induced by the electrospinning procedure and polarized UV light. To prove above opinion, the stacking of PDA chains inside the microfibers were characterized by the polarized Raman scattering spectrometer and fluorescence microscopy^[8,41–43]. Known to all, light with polarization direction parallel to the monomer is expected to be absorbed and thus induce polymerization. On the other hand, the light with polarization direction perpendicular to the monomer yield no or negligible absorption. [44, 45] So a linearly polarized laser beam at 632.8nm wavelength (He-Ne laser) was used as the incident laser beam for the Raman scattering spectra measurement. The polarized direction of the laser beam is either parallel ($\alpha = 0^\circ$) or perpendicular ($\alpha = 90^\circ$) to the microfiber. It is clearly that the Raman scattering intensity in the case of perpendicular polarization is stronger than that of parallel direction as shown in Figure 4a. The peaks at 2095 and 1453 cm^{-1} on the Raman scattering spectra were

typical evidences of the $C\equiv C$ and $C=C$ stretching vibrations, respectively.^[46] To dig out the structural orientation in details, we took the $C\equiv C$ stretching vibrations as the example. The Raman scattering intensity at 2095 cm^{-1} in the case of different polarization directions (angle α) of the incident laser beam is plotted in Figure 4b. Here the microfiber was polymerized with linearly polarized UV light ($\theta = 60^\circ$). The maximum Raman scattering intensity at 2095 cm^{-1} is noticed when α is about 150° or 330° , while the minimum intensity appears at about 60° or 240° . For comparison, the fluorescence intensity from the excited spot (point E1) at different α was also measured. As shown in Figure S6, the Raman intensity and FL intensity from point E1 were put together to demonstrate the ordered alignment of polymer main chains through illuminating with different polarization of UV light during polymerization. When the microfiber was polymerized with un-polarized UV light, the maximum Raman intensity from point E1 occurred when α is about 20° or 220° , the maximum FL intensity occurred when α is about 110° or 290° , the maximum fluorescence intensity happened in the case of minimum Raman intensity. Similarly, the maximum of Raman intensity occurred at α about 150° or 330° where the minimum of FL intensity happened when the fiber polymerized with polarized UV light ($\theta = 60^\circ$). Both Raman scattering and fluorescence intensity are not sensitive to the polarization direction of the incident light when the microfiber polymerized with circularly UV light. Therefore, we confirm that the ordered alignment of PDA main chains within the microfiber can be totally erased with a circular polarized UV light used in the polymerization procedure. As we know, the fluorescence emission is based on the absorption of the incident light, when the PDA main chains is parallel to the polarized direction of the excitation laser, its absorption will be higher resulting in higher fluorescence intensity. Whereas, the Raman scattering depends on the scattering of the incident light from the PDA main chains, the higher absorption will lead to lower scattering intensity. So the maximum fluorescence intensity happens in the case of minimum Raman scattering intensity. The consistence between the above fluorescence and Raman scattering intensity measurement confirms an ordered alignment of PDA main chains inside the microfibers.^[47, 48] To further verify this judgement, Figure S7 shows the change in Raman scattering intensity at 2095 cm^{-1} vs. angle α and fluorescence intensity for the microfibers polymerized using different θ ($\theta = 0, 90, 120$, and 150°). It is clear that the orientations of PDA main chains within the microfiber are almost the same as the polarization orientation (θ) of UV light. This result indicated that the predominant orientation of PDA main chains within the polymer microfiber could be easily and precisely controlled using only the polarization direction of the incident UV light.

At last, polarization properties of fluorescence emitting from the microfiber were investigated. By rotating the polarization analyzer placed before CCD detector, whose orientation is defined as angle (β) with respect to long axis of the microfiber, the polarization state of the out-coupled fluorescence from the Point E2 can be analyzed. For clarity we note that we are referring to the out-coupled light from the cylindrical surface (subsurface point E2). First we polymerized the microfiber with un-polarized UV light, as shown in Figure 5a, when the orientation angle (β) is 120° or 300° , the fluorescence reached the CCD detector is of maximum intensity. This angle was defined as a parameter $\beta_{\max}$. When the orientation angle is 30° or 210° ($\beta_{\min}$), the detected fluorescence intensity is minimum.

When the microfiber polymerized with linearly polarized UV light of $\theta=60^\circ$, $\beta_{\max}$ is 60° as shown in Figure 5b. The intensity ratio between the maximum ($I_{\max}$) and minimum ($I_{\min}$) value is observed as $\chi = I_{60^\circ}/I_{150^\circ}$, which is about 2.8. $\beta_{\max}$ is changed synchronously with the different polarization direction (θ) of the UV light used for polymerization as shown in Figure S8 (supporting information). What is more, as shown in Figure S9 (supporting information), the polarization orientation ($\beta_{\max}$) of the out-coupled fluorescence (from point E2) was found to be independent on the polarized direction of the excitation laser beam (angle α). However, the out-coupled fluorescence exhibited polarization isotropy (Figure 5c) when circularly polarized UV light was employed for the polymerization process. These phenomena clearly demonstrate that the polarization characteristics of the out-coupled fluorescence from the polymer microfiber can be easily and precisely controlled by the UV light during the polymerization procedure.

In summary, we demonstrated that the intrinsic alignment within the microfiber can be rigorously controlled by the polarization state of a UV light used in the polymerization procedure. The ordered intrinsic alignment of polymer main chains within the microfiber results in (1) relatively low propagation losses, (2) sensitivity of the fluorescence intensity to the polarization state of the illumination light and (3) unique polarization property of the fluorescence emitting from both the excitation and the emission point. Compared with the inorganic or semiconductor microfibers, novel PDA-embedded microfiber possesses several significant features. First, the chemical properties within the surface of PDA microfiber can be effectively tailored through simple surface modification. It is anticipated that the light-guiding performance of PDA microfiber could be easily modulated with various functional units. Secondly, the polymer matrix can host functional dopants ranging from metal oxides, fluorescent dyes to enzymes that can be used to tailor the optical properties of the PDA microfiber with great versatility. This flexible preparation method of the microfiber will be applicable for controlled polarization-sensitive devices, such as optical sensing, data storage, medical diagnostics, surveillance imaging and so on.

Experimental section

Materials

Monomer 10,12-pentacosadiynoic acid (PCDA, one of diacetylene) was purchased from Tokyo Chemical Industry Co., Ltd., and purified by dissolving in cyclopentanone and subsequently filtrating to remove polymer before used. Polystyrene (PS, $M_w = 260,000$) was purchased from J&K Chemical Co., Ltd. and used without further purification. All other solvents and reagents were of analytical grade and used as received.

Preparation of PDA-embedded electrospun microfiber

The typical procedure for fabrication of PDA-embedded electrospun microfibers is shown as follows. In brief, a chloroform solution containing 5 wt% of PCDA and 20 wt% of polystyrene (PS) was ejected at a continuous rate using a syringe pump through a stainless steel needle. A voltage of 13 kV was applied to the needle with a high voltage power supply and the feed rate of 0.5 mm/min was maintained with a syringe pump. A collector was placed at a distance of 10 cm from the tip of the needle to collect the fibers. Photo-

polymerization of the diacetylene-embedded fibers was then accomplished by irradiating with un-polarized UV light, or polarized UV light (linearly or circularly polarized) for 10 min. After UV irradiation, PCDA monomers polymerized into PDA polymers, the color of the white colored electrospun microfibers promptly changed to blue. Subsequently, thus polymerized microfibers were subjected to heating to 80°C for 10 min. Upon heating, the microfibers exhibit an intense color change, from blue to red, and the “red-phase” PDA microfibers show distinctive fluorescence (as shown in Figure S1).

Characterization

Scanning electron microscopy (SEM) was performed on a FEI Sirion200 system. X-Ray Diffraction (XRD) was characterized by using a MAC Science M18X X-photoelectron spectrometer. Raman scattering spectra were measured with a JY-ihR 550 spectrometer established on an IX-71 (Olympus) microscope. The light guiding along the microfibers and the spatially resolved fluorescence emission at fiber tip were characterized by home-built single-microfiber fluorescence imaging system (in Figure S5).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This research was carried out with funding from the National Key Basic Research Program of China (No. 2012CB921900, 2012CB922003, and 2013CBA01703), the National Natural Science Foundation of China (No. 51173176, 51273186, 21574120, 11374286, 61427818), the Fundamental Research Funds for the Central Universities (WK2060200012)

References

1. Wang W, Yang Q, Fan F, Xu H, Wang Z. Nano Lett. 2011; 11:1603. [PubMed: 21410216]
2. Liu N, Li Z, Xu H. Small. 2012; 8:2641. [PubMed: 22730154]
3. Li Q, Wei H, Xu H. Nano Lett. 2014; 14:3358. [PubMed: 24844583]
4. Ma L, Zhang Q, Ren P, Zhang X, Zhou H, Xu J, Li H, Shan Z, Wang X, Liao L, Xu H, Pan A. Nano Lett. 2014; 14:694. [PubMed: 24382206]
5. Gu F, Yang Z, Yu H, Xu J, Wang P, Tong L, Pan A. J Am Chem Soc. 2011; 133:2037. [PubMed: 21271702]
6. Zhuang X, Ning Z, Pan A. Adv Mater. 2012; 24:13. [PubMed: 22105863]
7. Guo P, Zhuang X, Xu J, Zhang Q, Hu W, Zhu X, Wang X, Wan Q, He P, Zhou H, Pan A. Nano Lett. 2013; 13:1251. [PubMed: 23421772]
8. Fasano V, Polini A, Morello G, Moffa M, Camposeo A, Pisignano D. Macromolecules. 2013; 46:5935. [PubMed: 23956464]
9. Gu F, Yu H, Wang P, Yang Z, Tong L. ACS Nano. 2010; 4:5332. [PubMed: 20738119]
10. Yang Z, Xu J, Wang P, Zhuang X, Pan A, Tong L. Nano Lett. 2011; 11:5085. [PubMed: 22011228]
11. Tian B, Zheng X, Kempa TJ, Fang Y, Yu N, Yu G, Huang J, Lieber CM. Nature. 2007; 449:885. [PubMed: 17943126]
12. Li Z, Bao K, Fang Y, Huang Y, Nordlander P, Xu H. Nano Lett. 2010; 10:1831. [PubMed: 20369891]
13. Guo P, Hu W, Zhang Q, Zhuang X, Zhu X, Zhou H, Shan Z, Xu J, Pan A. Adv Mater. 2014; 26:2844. [PubMed: 24677130]
14. Kim F, Ren G, Jenekhe S. Chem Mater. 2011; 23:682.

15. Persano L, Camposeo A, Pisignano D. *Prog Polym Sci.* 2015; 43:48.
16. Pan A, Yao L, Qin Y, Yang Y, Kim D, Yu R, Zou B, Werner P, Zacharias M, Gösele U. *Nano Lett.* 2008; 8:3413. [PubMed: 18754646]
17. Guo P, Xu J, Zhuang X, Hu W, Zhu X, Zhou H, Tang L, Pan A. *J Mater Chem C.* 2013; 1:566.
18. Xu J, Zhuang X, Guo P, Zhang Q, Huang W, Wan Q, Hu W, Wang X, Zhu X, Fan C, Yang Z, Tong L, Duan X, Pan A. *Nano Lett.* 2012; 12:5003. [PubMed: 22862798]
19. Wang X, Zhuang X, Yang S, Chen Y, Zhang Q, Zhou H, Guo P, Liang J, Huang Y, Pan A, Duan X. *Phys Rev Lett.* 2015; 115(1):027403. [PubMed: 26207503]
20. Das AJ, Lafargue C, Lebental M, Zyss J, Narayan KS. *Appl Phys Lett.* 2011; 99:263303.
21. Ta V, Chen R, Ma L, Ying Y, Sun H. *Laser Photon Rev.* 2013; 7:133.
22. Campoy-Quiles M, Lahii Y, Sakai H, Murata H. *Appl Phys Lett.* 2008; 92:213305.
23. Pagliara S, Camposeo A, Polini A, Cingolani R, Pisignano D. *Lab Chip.* 2009; 9:2851. [PubMed: 19967124]
24. Moynihan S, Lovera P, O'Carroll D, Iacopino D, Redmond G. *Adv Mater.* 2008; 20:2493.
25. O'Riordan A, Iacopino D, Lovera P, Floyd L, Reynolds K, Redmond G. *Nanotechnology.* 2011; 22:105602. [PubMed: 21289411]
26. Molenkamp WC, Watanabe M, Miyata H, Tolbert SH. *J Am Chem Soc.* 2004; 126:4476. [PubMed: 15070339]
27. Marco CD, Mele E, Camposeo A, Stabile R, Cingolani R, Pisignano D. *Adv Mater.* 2008; 20:4158.
28. Hu W, Chen Y, Jiang H, Li J, Zou G, Zhang Q, Zhang D, Wang P, Ming H. *Adv Mater.* 2014; 26:3136. [PubMed: 24536035]
29. Lin L, Mueller JPB, Wang O, Yuan G, Antoniou N, Yuan X, Capasso F. *Science.* 2013; 340:331. [PubMed: 23599488]
30. Garcia V, Bibes M, Bocher L, Valencia S, Kronast F, Crassous A, Moya X, Enouz-Vedrenne S, Gloter A, Imhoff D, Deranlot C, Mathur ND, Fusil S, Bouzehouane K, Barthélémy A. *Science.* 2010; 327:1106. [PubMed: 20075211]
31. Lee J, Balakrishnan S, Cho J, Jeon SH, Kim JM. *J Mater Chem.* 2011; 21:2648.
32. O'Carroll D, Lieberwirth I, Redmond G. *Nat nanotech.* 2007; 2:180.
33. Benedetto FD, Camposeo A, Pagliara S, Mele E, Persano L, Stabile R, Cingolani R, Pisignano D. *Nat nanotech.* 2008; 3:614.
34. O'Carroll D, Lieberwirth I, Redmond G. *Small.* 2007; 3:1178. [PubMed: 17450512]
35. Li X, Guo X, Wang D, Tong L. *Opt Commun.* 2014; 323:119.
36. Xiao Y, Meng C, Wang P, Ye Y, Yu H, Wang S, Gu F, Dai L, Tong L. *Nano Lett.* 2011; 11:1122. [PubMed: 21322600]
37. Kongkhlant T, Tashiro K, Kotaki M, Chirachanchai S. *J Am Chem Soc.* 2008; 130:15460. [PubMed: 18950171]
38. Liu Y, Pellerin C. *Macromolecules.* 2006; 39:8886.
39. Richard-Lacroix M, Pellerin C. *Macromolecules.* 2013; 46:9473.
40. Ma M, Liu J, Ni C, Martin DC, Chase DB, Rabolt JF. *ACS Macro Lett.* 2012; 1:428.
41. Sereda V, Sawaya MR, Lednev IK. *J Am Chem Soc.* 2015; 137:11312. [PubMed: 26278047]
42. Sheng G, Xue G, Cai J, Zou G, Li Y, Zhang Q. *Soft Matter.* 2013; 9:2512.
43. Rodríguez-Pérez J, Hamley LW, Squires AM. *Phys Chem Chem Phys.* 2013; 15:13940. [PubMed: 23852406]
44. Löwik DWPM, Shklyarevsky IO, Ruizendaal L, Christianen PCM, Maan JC, Van Hest JCM. *Adv Mater.* 2007; 19:1191.
45. Heuvel MVD, Löwik DWPM, Hest JCMV. *Biomacromolecules.* 2008; 9:2727. [PubMed: 18785773]
46. Filhol J, Deschamps J, Dutremez SG, Boury B, Barisien T, Legrand L, Schott M. *J Am Chem Soc.* 2009; 131:6979.
47. Venuti E, Valle RGD, Bilotti I, Brillante A, Cavallini M, Calò A, Geerts YH. *J Phys Chem C.* 2011; 115:12150.

48. Nagaveni NG, Gupta M, Roy A, Prasad V. J Mater Chem. 2010; 20:9089.

Author Manuscript

Author Manuscript

Author Manuscript

Author Manuscript

Figure 1.

Fabrication of microfibers with light guiding performance. a) Schematic representation of the preparation of PDA-embedded electrospun microfibers. b) Scanning Electron Microscopy characterization of the as-prepared PDA-embedded electrospun microfibers (left) and Cross-sectional SEM image of the broken microfiber (right). c) Fluorescence microscopy images of the same microfiber collected upon excitation at nine different positions. The excitation spot is defined as E1 (changeable), the emission spot at the end of the microfiber is defined as E2 (fixed), the distance between E1 and E2 is defined as propagation distance (L) (μm). d) $\text{Ln}(I_{E2}/I_{E1})$ vs. L and the exponential fit to the observed data.

Figure 2.

Controlled polarization-sensitivity to excitation light. a) Transmission bright-field optical image of a single microfiber (top), and fluorescence image (bottom) of the same microfiber under excitation of a focused laser beam. The excitation wavelengths is 532 nm. The polarization orientation of the excitation beam is defined as cross angle (α) with respect to the long axis of the microfiber (X-axis). This microfiber is polymerized under illumination of an un-polarized UV light. b) The change of emission intensity from the point E2 vs. angle α .

Figure 3.

The fluorescence emission intensity from the point E2 vs. angle (α). The microfibers were polymerized with linearly polarized UV light at different θ a) $\theta = 0^\circ$, b) $\theta = 60^\circ$, c) $\theta = 120^\circ$ and d) circularly polarized UV light.

Figure 4.

Orientation of PDA chains within the microfiber polymerized with linearly polarized UV light ($\theta=60^\circ$). a) Polarized Raman scattering spectra from the microfiber. The spectra are acquired with two polarization orientation (angles α) of incident light. The polarized direction of the laser beam is parallel ($\alpha = 0^\circ$, i) or perpendicular ($\alpha = 90^\circ$, ii) to the microfiber. The incident wavelength is 632.8 nm from the He-Ne laser. b) The Raman scattering intensity at 2095 cm^{-1} as a function of α .

Figure 5.

Controlled polarization properties of the fluorescence emission from point E2. a) The microfiber is polymerized under illumination of an un-polarized UV light. b) The microfiber is polymerized under illumination of an linearly polarized UV light ($\theta=60^\circ$). c) The microfiber is polymerized under illumination of a circularly polarized UV light.