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Self-Assembly and One-Dimensional Alignment of a Conducting Polymer Nanofiber in a Nematic Liquid Crystal

Sadaki Samitsu,*[†] Yoichi Takanishi, and Jun Yamamoto

Department of Physics, Faculty of Science, Kyoto University, Kitashirakawa, Sakyo, Kyoto 606-8502, Japan. [†] *Present affiliation: Functional Thin Films Group, Organic Nanomaterials Center, National Institute of Materials Science*

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Conducting polymer nanostructures have received much attention for scientific interest and industrial applications of organic electronics because their electro-optical properties closely relate to their morphology and dimensionality. In particular, a conducting polymer nanofiber is a promising candidate for nanoscale devices due to the characteristic carrier transport properties resulting from its one-dimensionality.[1] Among the wide variety of nanofiber production methods, a whisker method employing anisotropic polymer crystallization has potential advantages due to its facile production of a high-performance semicrystalline nanofiber by polymer self-assembly.[2−4] Large-scale alignment of nanofibers is important to the fabrication of nanofiber-based devices. While inorganic nanowires and carbon nanotubes have been successfully aligned on a large scale,[5,6] alignment of polymer nanofibers has been limited to a few micrometers.[7,8] Because of the weak interaction between polymers, the nanofibers themselves are highly flexible and easily become entangled during their growth. As a result, it is difficult to unidirectionally align them on a large scale. Application of liquid crystalline order to polymer self-assembly has remarkable potential for the organization of polymer nanostructures. Akagi and co-workers have extensively investigated in situ chemical and electrochemical polymerization in a liquid crystal and succeeded in the fabrication of superhierarchal structures of polyacetylenes.[9] Kato et al. produced a fibrillar structure consisting of a low-molecular-weight gelator via hydrogen bonding and alignment in a liquid crystal.[10] Although useful nanostructures have been organized by in situ polymerization and gelation, crystallization of a conducting polymer in a liquid crystal matrix is an alternative route to the construction of functional nanostructures and is expected to lead to high crystallinity and unique electro-optical properties. Here, we report the production of a conducting polymer nanofiber by a whisker method using anisotropic crystallization in a nematic liquid crystal. We successfully obtained large-scale alignment of the nanofibers. Moreover, we demonstrated polarized fluorescent emissions from unidirectionally aligned nanofibers under illumination by unpolarized light, which implies great potential for application in photo- and electroluminescent devices.

In this study, we chose a poly(3,3‴-didodecylquarterthiophene) (PQT12) as a model conducting polymer because the miscibility of the polymer in a nematic liquid crystal is higher than that of poly(3-alkylthiophenes). The chemical structure of PQT12 is shown in Figure 1a. Figure 1b shows a polarized UV−vis absorption spectra of PQT12 doped in a nematic liquid crystal E44. E44 is a commercial nematic mixture, which has a nematic phase at wide temperature range. The spectrum at 120 °C (the isotropic liquid phase) shows a single peak at 467 nm and no polarization dependence. The peak is ascribed to the $\pi-\pi^*$ band of PQT12, individually isolated in the solvent.[3b] The isotropic absorbance indicates no alignment of the PQT12. The spectrum at 70 °C (the nematic phase), on the other hand, shows a single peak with a large anisotropy. The polarized spectrum parallel to the director shows a much larger absorbance than the perpendicular. Since the transition moment of the $\pi-\pi^*$ band is located along the polymer chain,[11] the anisotropic absorbance indicates preferential alignment of the polymer chain parallel to the nematic director (i.e., the rubbing direction of the polyimide layer), which is similar to the behavior of other conductive polymers.[12] The temperature-dependent order parameter, S_{abs}, of PQT12 is calculated from the absorbance parallel and perpendicular to the nematic director (Figure 1c). S_{abs}, which was almost zero in the isotropic phase, gradually increased in the nematic phase with decreasing temperature. The curve is reminiscent of the temperature dependence of the order parameter for a liquid crystal molecule, suggesting that the liquid crystalline order induced alignment of the PQT12. An increase in liquid crystalline order with decreasing temperature would be expected to extend the polymer chain.[13] Indeed, the $\lambda_{\max}$ parallel to the director red-shifted by as much as about 20 nm at 60−102 °C (Figure 1d). The excluded volume interaction of liquid crystalline order and/or the anisotropic attractive interaction between a polymer and a liquid crystal molecule can stabilize polymer alignment along the director.[14] As a result, $\lambda_{\max}$ in the nematic phase (490 nm) was much longer than in toluene (464 nm) or chloroform (463 nm). In the lower temperature region (< 60 °C) of the nematic phase, the spectra parallel to the director exhibited a shoulder at about 580 nm. The absorbance at 580 nm emerges at 60 °C and rapidly increases with decreasing temperature (Figure 1e), which accompanies a blue shift of $\lambda_{\max}$. The increase in absorbance corresponds to the growth of a fibrillar structure observed with an optical microscope, as will be discussed in the following paragraph. The absorbance at $\lambda_{\max}$ originated from an isolated PQT12, while the absorbance at 580 nm was ascribed to PQT12 in a nanofiber. One of the authors has reported a similar increase in absorbance at 580−620 nm during the growth of a nanofiber of poly(3-alkylthiophene) (P3AT) in anisole solvent.[3b] The nanofibers highly restrict rotational motion of the polymer chain, providing an absorbance at longer wavelengths than for isolated PQT12.

In order to confirm the formation of nanofibers and their large-scale alignment, we observed the morphology of the sample using polarized optical absorption imaging. When the polarizer was placed parallel to the nematic director, the images showed fibrillar structures many hundreds of micrometers in length, unidirectionally aligned perpendicular to the director (Figure 2a). When the polarizer was perpendicular, on the other hand, the fibrillar structures had a much lower absorbance. Because the anisotropic absorbance closely relates to the fibrillar structure, the fibrillar structure was ascribed to aggregation as PQT12 chains oriented parallel to the director. It is notable that the fibrillar alignment was not parallel but normal to the director. In contrast, recent studies of in situ polymerization of other polythiophene derivatives in a nematic liquid crystal have reported that the local alignment of polymer nanotubes was

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*Corresponding author: Ph +81-29-851-3354 ext. 8326; Fax +81-29-852-7449; e-mail SAMITSU.Sadaki@nims.go.jp.

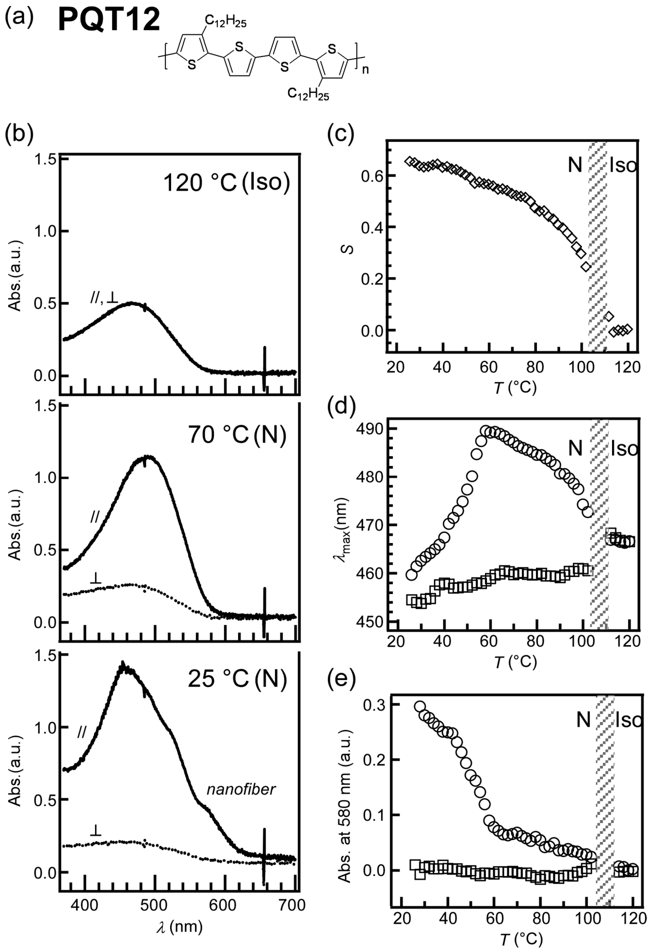


Figure 1. (a) Chemical structure of a conducting polymer, poly(3,3‴-didodecylquarterthiophene). The molecular weight of the polymer is 20 000−50 000. (b) Polarized UV−vis absorption spectra of PQT12 doped in a nematic liquid crystal. Solid and dotted lines show the spectra parallel and perpendicular to the rubbing direction, respectively. (c) Temperature dependence of order parameter S_{abs} of PQT12. (d) Temperature dependence of λ_{max} parallel (circles) and perpendicular (squares) to the rubbing direction. (e) Temperature dependence of absorbance at 580 nm parallel (circles) and perpendicular (squares) to the rubbing direction. The meshed region in (c)−(e) indicates the coexistence of an isotropic liquid phase (Iso) and a nematic phase (N).

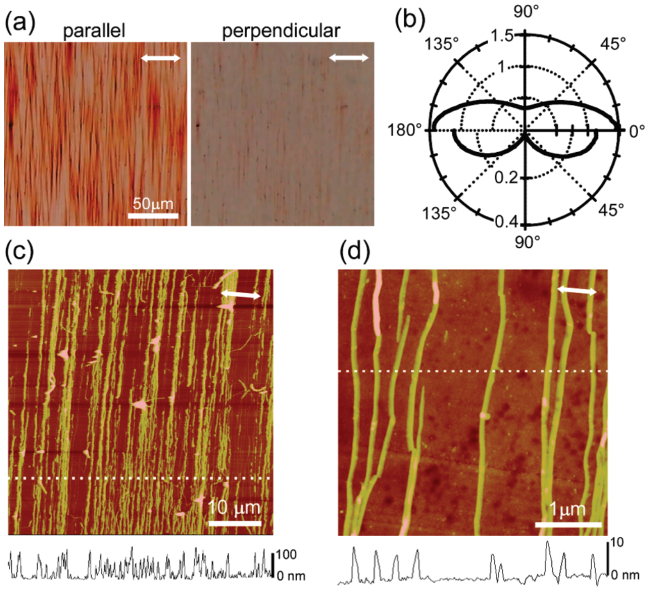
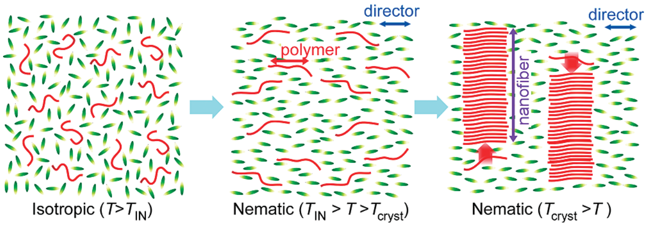


Figure 2. (a) Polarized absorption images of PQT12 nanofibers parallel and perpendicular to the rubbing direction at room temperature. White arrows indicate the rubbing direction of the polyimide layer. White scale bar is 50 μm. (b) Polar plot of the absorbance at λ_{max} (upper semicircle) and at 580 nm (lower semicircle). The temperature is 25 °C. The angles of 0° and 180° correspond to the rubbing direction. The absorbance at λ_{max} originated from an isolated PQT12, while the absorbance at 580 nm was ascribed to PQT12 in a nanofiber. S_{abs} at λ_{max} and at 580 nm were respectively determined to be 0.51 and 0.83. (c, d) AFM images of nanofiber bundles (c) and thin nanofibers (d) on a rubbed polyimide layer. Cross sections at the dotted line of the nanofiber bundles and the thin nanofibers, respectively, are shown below the images. Scale bar is 10 μm (c) and 1 μm (d).

Scheme 1. Schematic Illustration of Nanofiber Formation in a Nematic Liquid Crystal



parallel to the director.[9c] The different alignment with respect to the nematic director was caused by differing mechanisms of nanostructure formation: the former was by crystallization and the latter by polymerization. Polymer chains oriented parallel to the director crystallized into a stack of polymer chains, which formed nanofibers aligned normal to the director. The polar plot of the absorbance at λ_{max} and that at 580 nm (Figure 2b) both exhibited a maximum along the director (0° and 180°) and a minimum normal to the director (90°). S_{abs} at 580 nm was determined to be 0.83, which is much larger than at λ_{max} (0.51). This indicates that the polymer chains in the nanofiber were more aligned along the director than the isolated chains dispersed in a liquid crystal. This is probably due to restricted fluctuation of polymer chains in the nanofiber. The sequential process of nanofiber formation is illustrated schematically in Scheme 1. In an isotropic liquid phase, polymer chains are randomly oriented. In the higher temperature region (60−102 °C) of the nematic phase, the polymer chains are individually isolated and aligned along the director. The increase in liquid crystalline order during cooling makes the polymer chains more extended along the director, which enhances the delocalization of π orbitals and leads to a large red shift of λ_{max}. In the lower temperature region (<60 °C) of the nematic phase, the polymers self-assembled into a nanofiber, which was accompanied by an increase in absorbance 580 nm. The extended polymer chains that aligned along the director enhance the anisotropic growth of a stack of polymer chains, forming nanofibers normal to the director.

To further investigate the effect of liquid crystalline order on nanofiber formation, 4,4′-pentylcyanobiphenyl (5CB) was used as a nematic solvent instead of E44. In contrast to the unidirectional alignment of nanofibers in the nematic phase of E44, the nanofibers in 5CB were randomly oriented and caused strong light scattering by disturbing the liquid crystalline order. This strong light scattering made it impossible to obtain polarized UV−vis absorption spectra. This was because the T_{IN} of 5CB (ca. 35 °C) is much lower than that of E44 (ca. 102 °C), and PQT12 began to self-assemble into nanofibers in the isotropic phase of 5CB (at about 50 °C). Moreover, uniform films of PQT12 made by drop-casting or spin-coating on a rubbed polyimide layer showed no anisotropy (S_{abs} of 0.02−0.03, see Supporting Information). These results explicitly indicate that it was not the surface effect of the rubbed polyimide layer but the liquid

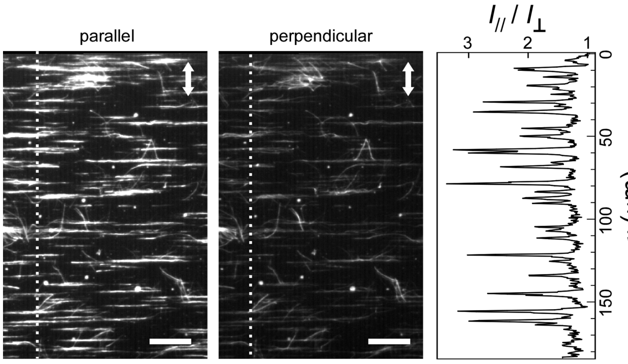


Figure 3. (Left) Polarized fluorescence images of the PQT12 nanofiber on a polyimide layer parallel and perpendicular to the rubbing direction. White arrows indicate the rubbing direction of polyimide layer. White scale bar is 50 μm. (Right) Cross-sectional profile of fluorescence anisotropy ratio $I_{\mathrm{para}}/I_{\mathrm{perp}}$ at the dotted line shown in the fluorescence images.

crystalline order in the bulk state that brought about the unidirectional alignment of the nanofibers.

After removing the liquid crystal matrix from the sample cell in which the nanofibers were formed, we observed the inner surface of the cell using an atomic force microscope (AFM). While an AFM image of a rubbed polyimide layer showed a smooth structure with several pits (see Supporting Information), the image clearly reveals large-scale unidirectional alignment of the nanofibers normal to the rubbing direction over 50 μm (Figure 2c). Several nanofibers were bundled, and the height of these bundles was about 100 nm. The nanofiber bundles formed a fibrillar structure, as observed by polarized absorption imaging. The unidirectional alignment contrasts strikingly with the random network morphology observed after spin-coating nanofiber solution from common organic solvents.[2-4] We enlarged the scan size of the image (5 × 5 μm) and found thin nanofibers aligned mostly normal to the rubbing direction (Figure 2d). We determined the height of the nanofibers to be about 10 nm.

Figure 3 shows fluorescent images of PQT12 nanofibers on a rubbed polyimide layer. The images clearly exhibit unidirectional alignment of fibrillar structures normal to the rubbing direction. Unpolarized light irradiation (450−500 nm) induced highly polarized fluorescence emission parallel to the rubbing direction, whose anisotropic ratio $I_{\mathrm{para}}/I_{\mathrm{perp}}$ reached values of 2−3. This anisotropy is due to good alignment of the polymer chains in the nanofiber. Polarized fluorescent emission of the unidirectionally aligned nanofibers under illumination by unpolarized light demonstrates great potential for application in photo- and electroluminescent devices.

In summary, we have developed a whisker method using a nematic liquid crystal solvent and achieved large-scale one-dimensional alignment of self-assembled conducting polymer nanofibers by crystallization in a nematic liquid crystal. The liquid crystalline order induced unidirectional alignment of polymer chains along the nematic director. Upon further cooling, the polymer chains crystallized nearly one-dimensionally and self-assembled into nanofibers consisting of stacked polymers that preserved their alignment. Anisotropic crystallization in a nematic liquid crystal enabled us to obtain macroscopic alignment of conducting polymer nanofibers normal to the director. AFM images revealed several nanofibers 10 nm in height aligned normal to the director and bundled into a one-dimensional fibrillar structure 100 nm in height. The unidirectional alignment of the nanofibers enabled the emission of polarized fluorescence with an anisotropy ratio $I_{\mathrm{para}}/I_{\mathrm{perp}}$ of 2−3 under illumination by unpolarized light.

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Supporting Information Available: Details in an experimental procedure, an optical microscope image of the nanofiber produced in 5CB, polarized UV−vis absorption spectra and polar plots of the absorbance in thin films, UV−vis absorption spectra in toluene and in chloroform, surface morphology of a rubbed polyimide layer. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Aleshin, A. N.; Lee, H. J.; Park, Y. W.; Akagi, K. *Phys. Rev. Lett.* **2004**, *93*, 196601. (b) Aleshin, A. N.; Lee, H. J.; Jhang, S. H.; Kim, H. S.; Akagi, K.; Park, Y. W. *Phys. Rev. B* **2005**, *72*, 153202. (c) Aleshin, A. N. *Adv. Mater.* **2006**, *18*, 17. (d) Hu, W. P.; Nakashima, H.; Furukawa, K.; Kashimura, Y.; Ajito, K.; Torimitsu, K. *Appl. Phys. Lett.* **2004**, *85*, 115.(e) Rahman, A.; Sanyal, M. K. *Phys. Rev. B* **2007**, *76*, 045110.

(2) (a) Merlo, J. A.; Frisbie, C. D. *J. Polym. Sci., Polym. Phys.* **2003**, *41*, 2674. (b) Merlo, J. A.; Frisbie, C. D. *J. Phys. Chem. B* **2004**, *108*, 19169.

(3) (a) Samitsu, S.; Shimomura, T.; Ito, K. *Thin Solid Films* **2008**, *516*, 2478. (b) Samitsu, S.; Shimomura, T.; Heike, S.; Hashizume, T.; Ito, K. *Macromolecules* **2008**, *41*, 8000.

(4) (a) Ihn, K. J.; Moulton, J.; Smith, P. *J. Polym. Sci., Polym. Phys.* **1993**, *31*, 735. (b) Kiriy, N.; Jahne, E.; Adler, H. J.; Schneider, M.; Kiriy, A.; Gorodyska, G.; Minko, S.; Jehnichen, D.; Simon, P.; Fokin, A. A.; Stamm, M. *Nano Lett.* **2003**, *3*, 707.

(5) (a) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001**, *291*, 630.

(6) (a) Kamat, P. V.; George, K.; Barazzouk, T. S.; Girishkumar, G.; Vinodgopal, K.; Meisel, D. *J. Am. Chem. Soc.* **2004**, *126*, 10757. (b) Lagerwall, J.; Scalia, G. *J. Mater. Chem.* **2008**, *18*, 2890.

(7) Mas-Torrent, M.; den Boer, D.; Durkut, M.; Hadley, P.; Schenning, A. P. H. J. *Nanotechnology* **2004**, *15*, S265.

(8) (a) Samitsu, S.; Iida, T.; Fujimori, M.; Heike, S.; Hashizume, T.; Shimomura, T.; Ito, K. *Synth. Met.* **2005**, *152*, 497. (b) Samitsu, S.; Shimomura, T.; Ito, K.; Fujimori, M.; Heike, S.; Hashizume, T. *Appl. Phys. Lett.* **2005**, *86*, 233103.

(9) (a) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 1683. (b) Goto, H.; Akagi, K. *Macromolecules* **2005**, *38*, 1091. (c) Goto, H.; Kawabata, K. *Macromolecules* **2008**, *41*, 4551.

(10) (a) Kato, T. *Science* **2002**, *295*, 2414. (b) Mizoshita, N.; Hanabusa, K.; Kato, T. *Adv. Mater.* **1999**, *11*, 392. (c) Mizoshita, N.; Hanabusa, K.; Kato, T. *Adv. Funct. Mater.* **2003**, *13*, 313. (d) Kitamura, T.; Nakaso, S.; Mizoshita, N.; Tochigi, Y.; Shimomura, T.; Moriyama, M.; Ito, K.; Kato, T. *J. Am. Chem. Soc.* **2005**, *127*, 14769.

(11) (a) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys.* **1987**, *25*, 1071. (b) Osterbacka, R.; An, C. P.; Jiang, X. M.; Vardeny, Z. V. *Science* **2000**, *287*, 839.

(12) (a) Zhu, Z.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *124*, 9670. (b) Fritz, K. P.; Scholes, G. D. *J. Phys. Chem. B* **2003**, *107*, 10141. (c) Lammi, R. K.; Fritz, K. P.; Scholes, G. D.; Barbara, P. F. *J. Phys. Chem. B* **2004**, *108*, 4598. (d) Link, S.; Hu, D.; Chang, W. −S.; Scholes, G. D.; Barbara, P. F. *Nano Lett.* **2005**, *5*, 1757.

(13) Tchemiak, A.; Solis, D.Jr.; Khatua, S.; Tangonan, A. A.; Lee, T. R.; Link, S. *J. Am. Chem. Soc.* **2008**, *130*, 12262.

(14) Matsuyama, A.; Kato, T. *Phys. Rev. E* **1999**, *59*, 763.