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Horizontal and Vertical Orientation of Polythiophenes by Electrochemical Polymerization in Magnetically Aligned Smectic Liquid Crystal

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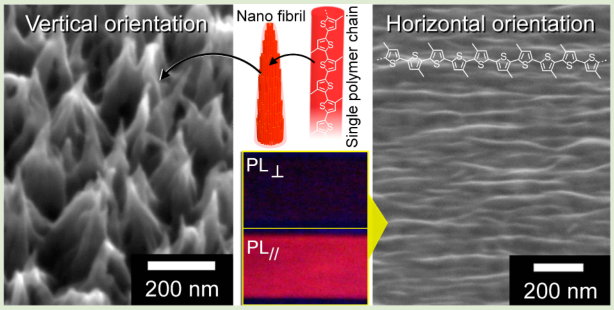
Supporting Information

ABSTRACT: Macroscopically highly oriented polythiophene derivative films are synthesized by electrochemical polymerization in a smectic liquid crystal reaction medium. Control of orientation direction of conjugated main chains is performed by use of magnetic field which is applied parallel, obliquely, and perpendicularly to the substrate electrodes to align the liquid crystal reaction medium.



Conjugated polymers have attracted much attention as a new class of semiconducting materials, which can be applied to organic electronic devices.[1−3] In this research field, orientation of molecules is of great importance because electronic and optical properties and anisotropy of conjugated polymers in the bulk state depend strongly on their molecular order. For example, in organic light-emitting diodes, a horizontal orientation of polymer chain to substrates is preferable to vertical orientation because emission from the polymer was parallel to the polymer chains. Besides, uniaxial orientation of polymer chains parallel to a substrate enables polarized emission.[4] In organic field emission transistors, a horizontal orientation of conjugated main chains with edge-on arrangement is ideal for high charge-carrier mobility parallel to a substrate.[5] On the contrary, in organic photovoltaics (OPV), high charge-carrier mobility perpendicular to electrodes is desirable for efficient charge separation to avoid recombination. Hence, vertical orientation of conjugated main chains or face-on molecular orientation to the electrodes is preferable for OPV.[6]

Recently, much effort has been made on alignment of polythiophenes. Polythiophenes are the most promising conjugated polymers because of their thermal and environmental stability and high electrical conductivity. However, simple unsubstituted polythiophenes have little processability because they are insoluble and infusible. For this reason, alkyl substituents are usually introduced to polythiophene backbones as side chains to enable solution and melt processing although longer alkyl chains decrease conductivity.[7] To date, such soluble and fusible polythiophenes have been aligned by various approaches, which include the whisker method,[8] rubbing,[9] tensile-drawing in polymer matrix,[10] the friction-transfer technique,[11] flow-coating,[12] directional solidification,[13] solvent vapor annealing,[14] and the Langmuir−Blodgett method.[15] On the other hand, alignment of poorly soluble polythiophenes, such as polythiophene, poly(methylthiophene), and poly(3,4-ethylenedioxithiophene), is more challenging. Some methods have been proposed for alignment of such poorly soluble polythiophenes, which include tensile drawing of polythiophene electrodeposited on flexible electrodes,[16] electrochemical polymerization with microporous templates,[17] and lyotropic columnar mesophase and themotropic mesophase templates.[18] However, these methods limit the choice of substrates and alignment directions with macroscopic uniformity.

To date, liquid crystals (LCs) have been used as templates for alignment of conjugated polymers.[18,19] Electrochemical polymerization in liquid crystal electrolyte solution was first developed in 2000.[20] Recently, macroscopic and horizontal orientation of conjugated polymers has been performed by using oriented nematic liquid crystal (NLC) and smecticA (SmA) liquid crystal (LC) reaction media.[21] In the present study, a series of thiophene monomers were used for electrochemical polymerization in SmA LC media, which are magnetically oriented parallel, perpendicularly, and obliquely to substrates. This method enables anisotropic growth of conjugated main chains, which are aligned along the director of the LC media. The resulting polymer films with parallel orientation to the substrates exhibited polarized absorption with macroscopically uniform alignment, some of which also show highly polarized emission. Furthermore, polymerization

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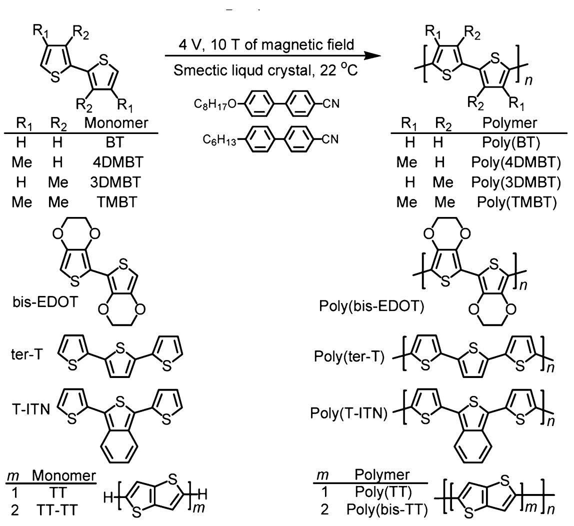
in vertically and obliquely oriented SmA LC media provided vertically and obliquely aligned polymer nanofibrils, respectively. This simultaneous orientation−polymerization is a unique and convenient method for controlling molecular orientation of poorly soluble polythiophenes.

A SmA LC medium was prepared from 4-cyano-4′-*n*-hexylbiphenyl (6CB) and 4-cyano-4′-*n*-octyloxybiphenyl (8OCB) (the mixing ratio = 4/6 (w/w)) according to the reported method.[21b] Examined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM), the LC medium was confirmed to show SmA phase at around room temperature on a cooling process (Figures S1 and S2, Supporting Information). A series of thiophene monomers, 2,2′-bithiophene (BT), 3,3′-dimethyl-2,2′-bithiophene (3DMBT), 4,4′-dimethyl-2,2′-bithiophene (4DMBT), 3,3′,4,4′-tetramethyl-2,2′-bithiophene (TMBT), 2,2′-bis(3,4-ethylenedioxythiophene) (**bis**-EDOT), 2,2′;5′,2″-terthiophene (ter-T), 1,3-di(2-thienyl)isothianaphthene (T-ITN), thieno[3,2-*b*]thiophene (TT), and 2,2′-bithieno[3,2-*b*]thiophene (bis-TT), were electropolymerized in SmA phase of the LC medium under 10 T of magnetic field (Scheme 1). The magnetic field is applied parallel and perpendicularly to the substrate electrode prior to and during electrochemical polymerization at ambient temperature (∼22 °C) (Figure 1). The detailed procedure is described in the Supporting Information.

Scheme 1. Electrochemical Polymerization in SmA LC



Generally, in the SmA phase, molecular orientation is limited in a meso-scopic scale to form a polydomain structure. However, such a strong magnetic field can orient LC molecules uniformly on a macroscopic scale because of the diamagnetic anisotropy effect of aromatic mesogens in the LC molecules.[22] 1 T of magnetic field is strong enough to orient the LC in this study. However, 10 T of magnetic field was used for quick and complete alignment of the SmA LC. Thus, a uniformly aligned anisotropic reaction environment was constructed for subsequent electrochemical polymerization.

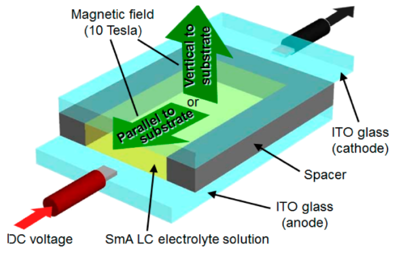


Figure 1. Illustration of the electrochemical polymerization in a magnetically aligned SmA LC medium.

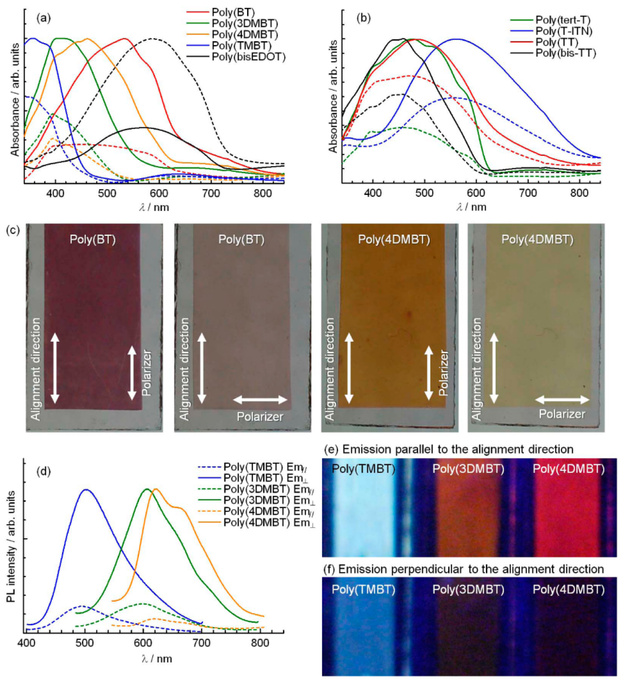


Figure 2. Linearly polarized absorption spectra of the polymer films prepared in the horizontally aligned smectic LC media (a and b) with polarization directions parallel (solid) and perpendicular (dashed) to the LC director. Photos of poly(BT) and poly(4DMBT) film (1 cm × 2 cm) with different polarizer directions (c). Polarized PL spectra of the poly(4DMBT), poly(3DMBT), and poly(TMBT) films with polarized emission direction parallel (solid) and perpendicular (dashed) to the LC director (excited with unpolarized light) (d). Photos of polarized PL emission from the poly(TMBT), poly(3DMBT), and poly(4DMBT) films (1 cm × 1.5 cm) with polarization direction parallel (e) and perpendicular (f) to the LC director.

The polymer films prepared in the SmA LC exhibited $\pi-\pi^*$ transition absorption bands around the ultraviolet, visible, and near-infrared region. The polymer films prepared with the magnetic orientation parallel to the substrate showed polarized absorption in the $\pi-\pi^*$ transition absorption bands (Figure 2a and b). The polymers, except for poly(bis-EDOT), have more intense polarized absorption parallel to the magnetic orientation than that with perpendicular direction. The optical anisotropy of the polymer films is macroscopically uniform (Figure 2c). Generally, linear conjugated polymers have $\pi-\pi^*$ optical transition dipole moments along their conjugated main chain.[23] Accordingly, the conjugated main chains of the polymers were aligned parallel to the direction of magnetic orientation, namely, the director of the SmA LC used. These results are consistent with the results from polymer films prepared in an NLC medium which was aligned by the rubbing method.[19] On the other hand, poly(bis-EDOT) showed stronger absorption polarized perpendicularly to the direction of the magnetic orientation than the parallel polarized absorption, which is consistent with previously reported results of poly(ter-EDOT).[21b] The discrepancy of alignment directions between poly(bis- and ter-EDOT) and other polymers may be due to the nonrodlike molecular shapes of bis- and ter-EDOT which cause anisotropic excluded volume effects different from other monomers.

Parallel polarized absorption of the polymers showed longer absorption maximum wavelengths than those with perpendicular polarization. This indicates that the direction of lower-energy optical transition moments is more parallel to the direction of magnetic alignment than that of higher-energy ones. The polymers show absorption dichroic ratios ranging from 3.9 to 1.3, which depend on the parent monomers. Even the polymers with the same chemical structure, such as poly(BT) and poly(ter-T), poly(3DMBT) and poly(4DMBT), and poly(TT) and poly(bis-TT), have different dichroic ratios. The dichroic ratios of conjugated polymers reflect the angle of the optical transition dipole moment relative to the polymer chain axis director as well as order parameter of conjugated main chains.[23] Therefore, the dichroic ratios cannot evaluate the real order parameters of the polymers.

Among the horizontally oriented polymers, poly(TMBT), poly(3DMBT), and poly(4DMBT) show polarized emission with excitation by unpolarized light. The poly(methyl substituted bithiophene)s show stronger photoluminescence (PL) in parallel direction to the alignment direction than that in the perpendicular direction (Figure 2d, e, and f). Poly(TMBT) showed white green light with an emission band at around 500 nm which covers the broadly visible region (400−700 nm). Poly(3DMBT) and poly(4DMBT) showed orange and red light with emission bands at 605 and 620 nm, respectively, despite the same chemical structure. The different conjugation lengths between poly(3DMBT) and poly(4DMBT) have been discussed elsewhere.[24] As well as polarized absorption, emission maximum wavelengths of parallel emission of the polymers are longer than those of perpendicular emission. Poly(TMBT), poly(3DMBT), and poly(4DMBT) have dichroic ratios of emission of 5.3, 4.9, and 10.3, respectively. These dichroic ratios of emission are larger than those of absorption. This result indicates exciton migration from arbitrary excited sites to well-aligned conjugated sites which have lower-energy excited states.[25] As mentioned above, the lower-energy absorption transition moments lie more parallel to the alignment direction than the higher-energy ones. Through PL, radiatively excited sites in the conjugated polymer chains can diffuse intra- and intermolecularly to the lower-energy states before emission.

Mesoscopic optical anisotropy of the horizontally oriented poly(4DMBT) film was examined by the POM and polarized fluorescent microscopy. Figure 3a and b shows POM images of the poly(4DMBT) film with different angle of crossed Nicols to the alignment direction. When the angle between the alignment direction and analyzer (and polarizer) is 45°, the polymer film shows a bright-field image without any optical texture. The bright-field color is not due to the color of the polymer itself but due to the retardation effect. When the angle is 0° or 90°, the polymer film shows a dark-filed image. This supports that the polymer chains are aligned in one direction to show birefringence. Furthermore, polarizing fluorescence microscopy reveals that the polymer film shows different brightness of fluorescence images, which depends on the analyzer direction (Figure 3c and d). Strong red emission from the polymer film was observed when the analyzer direction was parallel to the alignment direction, while little emission was observed when the analyzer and alignment direction was in the perpendicular position. In these images, no optical texture was observed, also indicating uniform alignment of the polymer chains in mesoscopic scale.

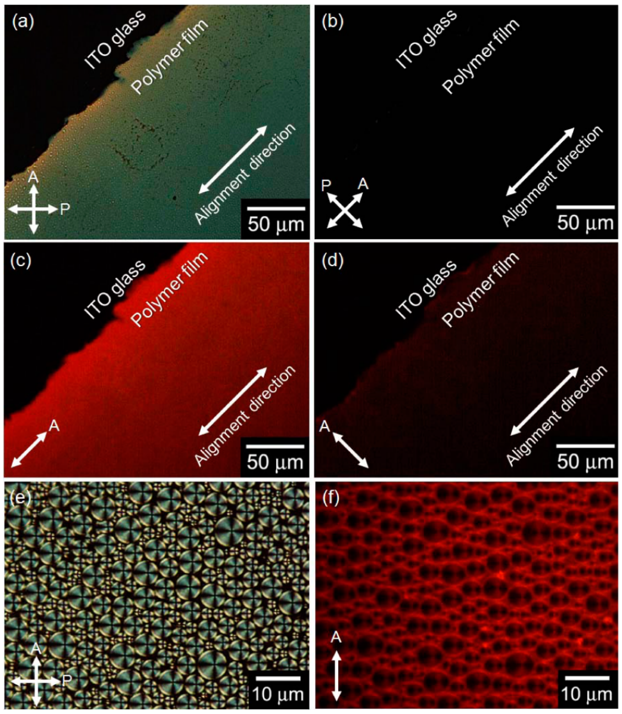


Figure 3. Polarizing optical microscopic images of horizontally aligned poly(4DMBT) (a and b) and unoriented poly(4DMBT) (e) and polarizing fluorescence microscopic images of horizontally aligned poly(4DMBT) (c and d) and unoriented poly(4DMBT) (f).

Generally, a SmA LC phase without any alignment treatment shows polydomain textures such as focal-conic-fan shape and polygonal textures (Figures S1a, b, and c, Supporting Information). At the domain boundaries, the LC molecular orientation is discontinuously changed and considered as the defect plane. Poly(4DMBT) film prepared in an unoriented SmA LC medium exhibited polydomain focal-conic-fan shaped texture under crossed Nicols, which is similar to that of the SmA LC medium (Figure 3e). In polarizing fluorescence microscopy images, the poly(4DMBT) film also shows focal-conic-fan shaped texture with red emission (Figure 3f). This indicates that the direction of conjugated polymer chains was locally oriented in the domains like the SmA LC molecular order. The contrast of the color and emission in the focal-conic-fan texture in Figure 2e and f indicates confocal orientation of the polymer chains in the focal-conic domains and random orientation of the polymer chains between the domains. On the contrary, no optical texture of the polymers prepared in the horizontally aligned SmA LC indicates perfect uniform alignment of the polymer chains without any domain boundary. SEM observations revealed that the horizontally aligned poly(4DMBT) film showed nanoscopically oriented surface morphology, which has aggregated nanofibrils aligned in the direction of magnetic orientation (Figure 4a). Thus, horizontal alignment of poly(4DMBT) is performed from the nanoscopic to macroscopic scale. On the other hand, poly(4DMBT) film prepared in the vertically aligned SmA LC has vertically grown nanofibrils, which closely packed on its surface (Figure 4b). The nanofibrils have a few tens nanometer of diameter, some of

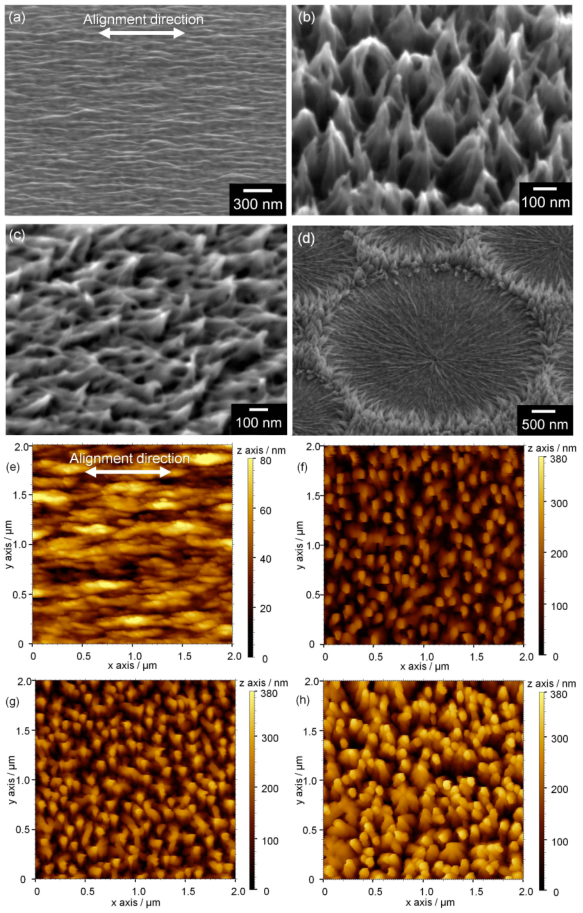


Figure 4. Scanning electron microscopic images of horizontally (a) and vertically (b) and obliquely (c) oriented and unoriented (d) poly(4DMBT) films taken from 45°. Atomic force microscopic images of horizontally (e) and vertically (f, g, and h) oriented poly(4DMBT) films.

which aggregate to form thicker fibrils. The distinct difference between the surface nanostructures of vertically and horizontally aligned poly(4DMBT) indicates strong directional dependence of polymer elongation. In the POM observation of the vertically aligned poly(4DMBT) film, no transmitted light was observed with any directions of the crossed Nicols. The polymer film showed no polarized absorption when the incident light was normal to the film. However, the film exhibited polarized absorption with oblique incident light. These results suggested that the conjugated main chains were aligned along the nanofibrils, namely, vertical to the substrate. Furthermore, poly(4DMBT) prepared in the obliquely (45° from the substrate) oriented SmA LC showed obliquely aligned nanofibrils (Figure 4c). The obliquely aligned poly(4DMBT) showed no optical anisotropy in the view from the alignment direction but showed polarized absorption in perpendicular direction to the alignment (Figure S9, Supporting Information). The poly(4DMBT) with focal-conic texture showed confocal orientation of the polymer nanofibril on the surface of the domain, as expected from its POM images (Figure 4d).

An atomic force microscopy (AFM) image of the horizontally oriented poly(4DMBT) showed grooves along the magnetic alignment direction due to uniaxially aligned nanofibrils (Figure 4e). On the contrary, the AFM images of the vertically oriented poly(4DMBT) film show vertically oriented nanofibrils to form rougher surface than the horizontally oriented polymer film. The roughness of the vertically aligned poly(4DMBT) increases with polymerization time (Figure 4f, g, and h). Electrochemical polymerization for 5 min, 10 min, and 20 min affords the polymers with fibril height of around 260 nm, 320 nm, and 370 nm, respectively. This suggests that the height of vertically oriented nanofibrils can be controlled over several hundred nanometers by changing the polymerization time. Recently, it has been reported that oriented conjugated polymers have higher carrier mobility along the orientation direction of conjugated main chains than perpendicular direction.[26,27]

Thus, the conjugated polymer nanofibrils in this study are expected to have high carrier mobility along the fibril axis. The vertically aligned insoluble polythiophene nanofibril surface is a promising candidate for donor materials in OPV. This is because a large surface area and expected high carrier mobility normal to the substrate may perform efficient charge separation in the donor−acceptor interface in OPV. Alternatively, obliquely oriented polythiophene nanofibrils may be better than vertically oriented ones from the viewpoint of optical absorption efficiency normal to the substrate. Furthermore, subsequently available solution processes onto the polymer film facilitate easy fabrication of devices.

Other polymers in this study also showed characteristic surface morphology, which depended on the magnetic alignment directions (Figure S4 and S5, Supporting Information). Previously, it has been reported that in electrochemical polymerization applying a magnetic field parallel to the substrates leads to face-on molecular orientation of the resulting polythiophene films.[19] However, orientation of polymer chain direction was not achieved with the magnetic field. On the other hand, in this study, even without magnetic field polymer chain orientation along the LC director was performed. Therefore, the macroscopic orientation of the polymers is carried out not by the magnetic field itself but through simultaneous polymerization−orientation in the magnetically aligned SmA LC anisotropic media.

This SmA LC mediated electrochemical polymerization combined with magnetic LC orientation is a unique and convenient method for macroscopic and nanoscopic orientation of conjugated polymer films.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental details and Figures S1−S9. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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