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Communications to the Editor

Visualization of Nematic Liquid Crystal Director by Alignment of π-Conjugated Polymer Nanotubes

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Electrochemical polymerization and chemical oxidative polymerization have recently been employed to synthesize organic conjugated polymer nanotubes and nanofibers.[1] Polyaniline (PAni) nanotubes have been synthesized by a self-assembly method in the presence of camphorsulfonic acid[2] and by a template method,[3] while hollow spheres of PAni have been synthesized by a self-assembly method in the presence of perfluorooctanesulfonic acid (a dopant) and a soft template providing superhydrophobicity.[4] Poly(3,4-ethylenedioxythiophene) (PEDOT), a promising conducting polymer with industrial applications, has been similarly prepared in nanotube form by electrochemical polymerization[5] and chemical oxidative polymerization.[6] PEDOT nanotubes have been examined for practical application as soft actuators and in drug delivery systems.[7] A reverse cylindrical micelle-mediated interfacial polymerization approach has also been used to prepare solid nanorods of PEDOT.[8]

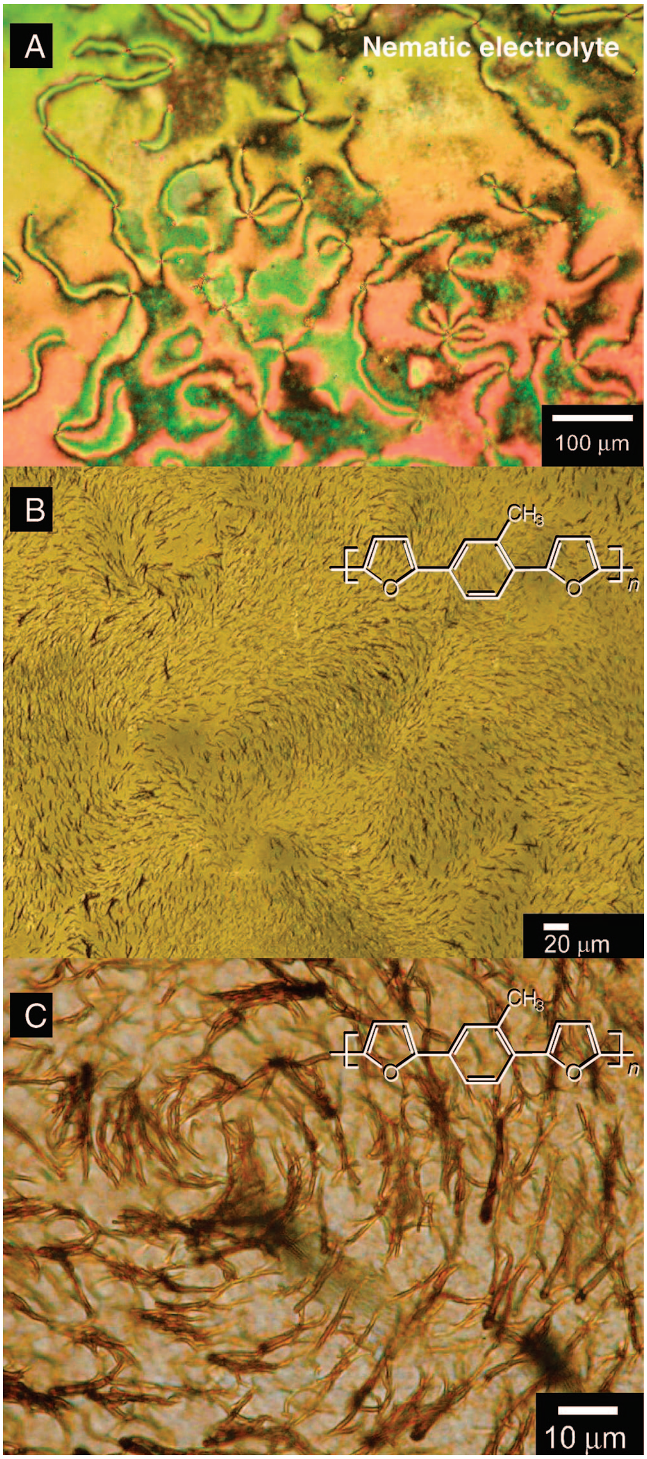

Figure 1. (A) Polarizing optical microscopy (POM) image of 6CB-based nematic electrolyte containing the monomer. (B, C) POM image of polymer (poly[2,5-di(2-furyl)toluene]) prepared by electrochemical polymerization in nematic electrolyte.

The efficient preparation of polymer ordered structure is thus of considerable interest for a range of applications. A promising means of controlling the macrostructure of polymers in the preparation of polymers is through the use of an ordered reaction field. Thermotropic liquid crystal (LC) displays a characteristic optical texture over a certain temperature range, and nematic LC in particular exhibits a Schlieren optical texture under appropriate conditions. The primary feature of molecular organization in nematic LC is the orientational order of the molecular axis, where the average direction of the long axes defines the director (n), which may be treated as a vector. The Schlieren texture, which can be observed by polarized optical microscopy (POM), appears as a brushlike pattern, reflecting the disclinations and directors of individual LC molecules in the system. LC solvents have been employed for more than 20 years for the preparation of highly oriented polyacetylenes using the Ziegler−Natta catalytic system,[9] and the polyacetylene films thus prepared display a high degree of fibril orientation. Polypyrrole (PPy) with an ordered structure has recently been prepared through the electrochemical polymerization of pyrrole (Py) in nematic LC.[10] The electrochemical polymerization of pyrrole,[11] bithiophene,[12] and thiophene derivatives[13] has also been performed using cholesteric LC electrolytes, while PEDOT has been synthesized using a DNA LC solution to yield an optically active

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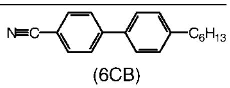
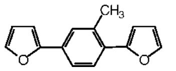
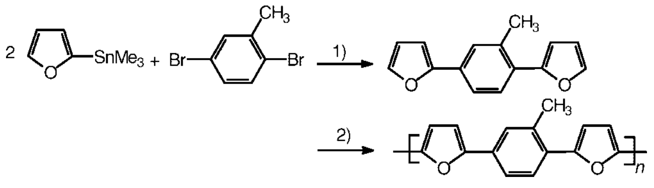
Table 1. Constituents of Nematic Electrolyte

Nematic Liquid crystal solvent	 (6CB)
Supporting salt	$(C_4H_9)_4NClO_4$ (TBAP)
Monomer	

Scheme 1. Synthesis of the Polymer: (1) [Pd(PPh$_3$)$_4$], Toluene; (2) Electrochemical Polymerization in Nematic LC Electrolyte



product.[14] DNA was employed for inducing helicity in the polythiophene derivatives for biosensor applications.[15] Template polymerizations for nanohybrids of PEDOT/β-1,3-glucane schizophyllan[16] and PEDOT/lipid assemblies[17] have also been reported.

The radical polymerization of vinyl monomers in a micelle field has been studied as a means of controlling the structure and particle size of polymers. The electrochemical preparation of PAni[18] and PEDOT[19] in micelle lyotropic LC[20] results in molecular imprinting during polymerization, and three-dimensional specific surface morphologies have been achieved for PPy[10] and polyacetylene[21] prepared in cholesteric LC. The uniform alignment of carbon nanotubes has also been reported using discotic LC through the insertion of single-wall nanotubes in the molecular order of the columnar phase.[22] LC materials are thus widely employed in chemistry and physics as molecular templates for the synthesis of polymers with supramolecular order.

In the present study, furan-based π-conjugated polymer nanotubes are prepared by electrochemical polymerization in nematic LC electrolyte to afford polymer nanotubes aligned with the nematic LC director. This method allows visualization of LC directors as vectors defined by the alignment of organic polymer nanotubes.

The monomer was synthesized by the Stille coupling reaction with the aid of a Pd(0) catalyst as follows (Scheme 1). 2-(Tributylstannyl)furan and 1,4-dibromotoluene were reacted in toluene solution in the presence of [Pd(PPh$_3$)$_4$] for 24 h. The solvent was then evaporated, and the crude product was purified by column chromatography (silica gel, *n*-hexane) to afford 2,5-di(2-furyl)toluene as a colorless oil. The LC electrolyte was subsequently prepared by the addition of tetrabutylammonium perchlorate (TBAP) (0.52 mg, 1.5×10^{-3} mmol) to 4-cyano-4′-hexylbiphenyl (6CB) (125.8 mg, 4.8×10^{-1} mmol), a well-

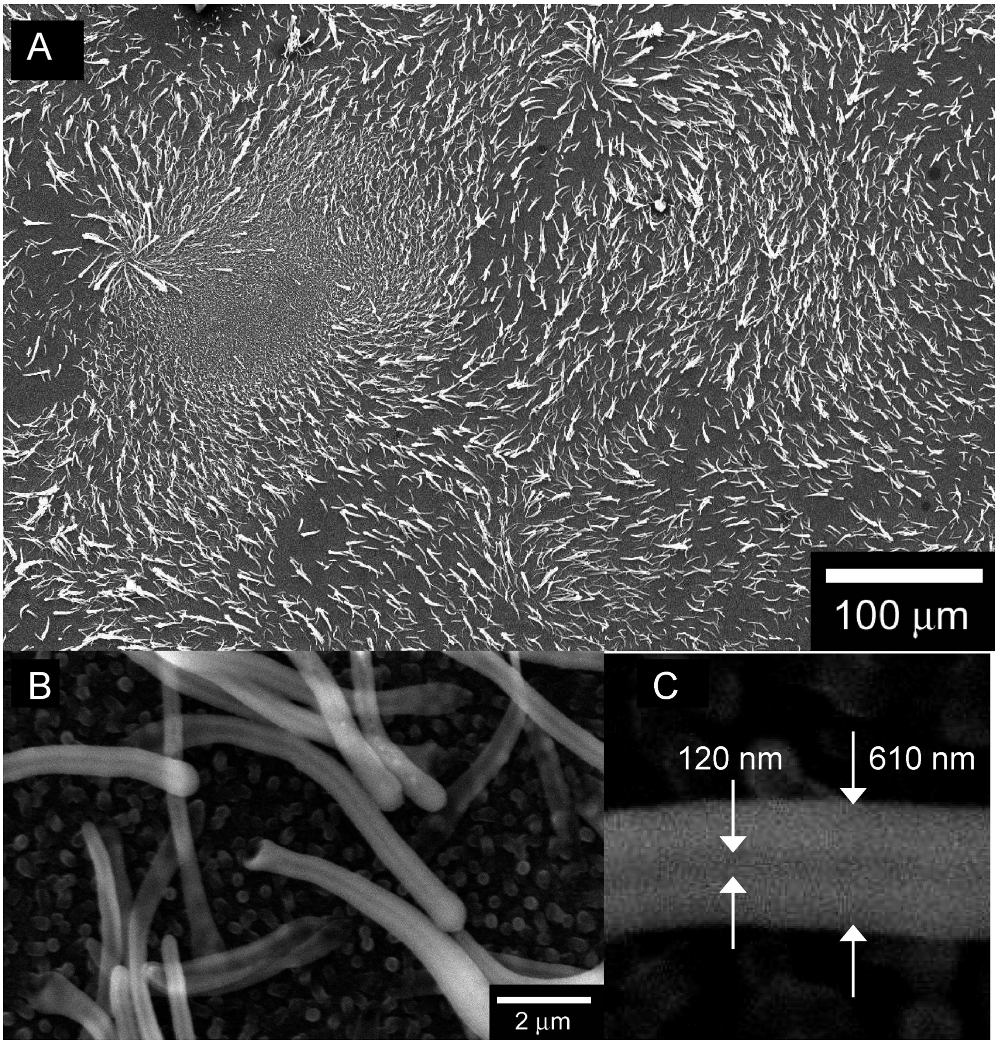


Figure 2. SEM images of the polymer.

known nematic LC. Liquid crystallinity was confirmed to be maintained after the addition of TBAP (as a supporting salt) and the monomer (2,5-di(2-furyl)toluene) (2.9 mg, 0.013×10^{-3} mmol). The molecular structures of the constituents of the LC electrolyte system are shown in Table 1. The mixed system exhibited a Schlieren texture at room temperature, typical of the nematic phase, as shown in Figure 1A. 6CB is a thermotropic LC that acts as a fluid solvent in this system, and the supporting salt provides ionic conductivity. The mixture of LC, monomer, and supporting salt can thus be used as an electrolyte for electrochemical polymerization in place of normal systems containing a supporting salt in isotropic solution.

The electrolyte solution was heated in a vial (internal diameter: 5 mm) to 40 °C to completely dissolve the supporting salt and monomer in 6CB as the LC solvent. Visual inspection by POM confirmed that the nematic electrolyte containing the monomer exhibited thermotropic nematic liquid crystallinity at room temperature. The vial was then set in a vessel saturated with moisture vapor for 10 min to introduce trace quantities of water into the electrolyte. Electrochemical polymerization was carried out using this monomer-containing nematic electrolyte by injecting the mixture between sandwiched indium tin oxide (ITO)-coated glass electrodes separated by a Teflon sheet (thickness: 0.19 mm). This sandwich-cell electrochemical polymerization method is similar to the fundamental preparation technique for LC displays and allows electrochemical polymerization in LC with low ionic conductivity. A voltage of 4 V was subsequently applied to the cell. The optical texture of the nematic LC mixture remained unchanged upon voltage application. The polymerization temperature was maintained constant at 22 °C through the use of a custom-made temperature control stage with Peltier element in order to preserve the nematic phase. After 15 min, an insoluble and infusible thin polymer film had coated the anode side of the ITO electrode. The nematic electrolyte after polymerization retained its LC character at 22 °C, indicating that liquid crystallinity was maintained throughout the polymerization reaction. The polymer was finally washed with acetone.

The polymer thus prepared exhibits birefringence and a characteristic Schlieren texture with 2- and 4-fold brushes similar to that of nematics under POM observations (Figure 1B). This texture contrasts with that of polymers prepared by electrochemical polymerization in acetonitrile (isotropic), which do not exhibit birefringence. The polymer prepared by the present method therefore appears to grow along the direction of the nematic phase during polymerization to form a texture similar to that of nematic LC. The brushes of the Schlieren texture on the film visually rotate with rotation of the POM analyzer, as generally observable for nematic LC, indicating that the present polymer has Schlieren-like molecular ordering. The film surface also displays a characteristic textile-like structure along the Schlieren texture under POM observations (Figure 1C). Scanning electron microscopy (SEM) observations further reveal that the furlike structure consists of short standing fibers and long (>800 nm) fibrils aligned horizontally along the Schlieren texture, that is, parallel to the substrate and the nematic LC director (Figure 2A,B). The polymer fibrils are hollow, having an outer diameter of 370−925 nm and inner diameter of 75−260 nm. An image of a typical fiber is shown in Figure 2C. The dimensions of the fibers are comparable to those of chemically synthesized PEDOT[23] and PAni nanotubes. It is likely that some of the nanofibers may be occluded to excessive wall thickening during growth.

The monomer employed in this study has good polymerization activity and is highly rigid. These properties, and the formation of π-stacking in the conjugated polymer, result in a mode of polymer aggregation that produces a tubular fibril structure during electrochemical growth. The presence of a small amount of water in the nematic electrolyte aids formation of the tubular structure, similar to the mechanism of PEDOT nanotube and PAni nanotube formation in water or a water-based microemulsion system.[24] The monomer/water interface is considered to be important in the formation of nanotubes in such systems. Although the nematic LC directs the growth of the polymer parallel to the director continuum, the formation of higher-order structures such as nanotubes is more closely related to chemical interactions with the medium itself, while the insolubility of the polymer in the nematic LC electrolyte facilitates phase separation.[25]

Investigations of the interaction between nematic or cholesteric LC matrices and conjugated polymers such as polyacetylene,[9] polythiophene derivatives,[13] and PEDOT[26] have indicated that π-conjugated polymers follow the order of the LC host. That is, although the molecular structure of the polymer differs from that of the nematic electrolyte, the arrangement of polymer nanotubes follows the nematic structural order. The insolubility, infusibility, and stiffness of the polymer are considered to prevent reorganization after the polymerization process by effectively locking the order of polymer tubes oriented according to the nematic order. The surface structure of the polymer is maintained even after several washes with organic solvents. Reorganization of the polymer nanotubes in the nematic LC after polymerization is therefore considered to be negligible.

Other conducting polymers such as PPy or PAni may also form nanotubes upon electrochemical polymerization in thermotropic nematic LC. However, it has been reported that PPy prepared in nematic LC shows a fibril structure without the formation of tubes,[10] while the polymerization of PAni in nematic LC does not afford free-standing films.[27] Polymers prepared from other monomers will have dissimilar characteristics in terms of conductivity, crystallinity, and molecular structure, and it thus appears likely that appropriate reactivity and physical properties are required in order to form nanotubes.

In summary, the electrochemical polymerization method presented in this study affords a polymer that visually reproduces the LC pattern through the arrangement of polymer nanotubes, and the surface structure of the polymer is maintained even after washing. As LC materials exhibit a range of optical textures reflecting the molecular orientation at both the molecular and macroscopic scales, many opportunities still exist for polymer structural control through appropriate application of shear stress, magnetic field, or linearly polarized light. The present polymerization method can also be expected to be useful for investigating LC phase structures.

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