

Fabrication of Large-scale Drop-cast Films of π -conjugated Polymers with Floating-film Transfer Method

Dauendorffer Arnaud, *Rajiv K. Pandey, Syougo Miyajima, **Shuichi Nagamatsu, Rajiv Prakash, ***Wataru Takashima, Shuzi Hayase and Keiichi Kaneto

Graduated School of Life Science and Systems Engineerings, Kyushu Institute of Technology, Japan

*School of Material Science and Technology, Indian Institute of Technology, Banaras Hindu University, India

**Department of Computer Science and Systems Engineerings, Kyushu Institute of Technology, Japan

***Research Center for Advanced Eco-fitting Technology, Kyushu Institute of Technology, Japan

Fax: 81-93-695-6235, e-mail: watakashi@lsse.kyutech.ac.jp

Large-scale drop-cast films of π -conjugated polymers such as polythiophene derivatives and polyfluorene-based copolymers have been formed on a liquid-substrate with one-step deposition of Floating-film Transfer Method (FTM). Centimeter-scale uniform cast films could be obtained. Relative sharp vibronic structure was found in the Absorption spectra of FTM films as compared to those in spin-coated ones. FTM provides concentrically oriented films of a polymer having thermotropic liquid crystal characteristics. Comparative study of AFM topography with absorption spectra revealed that the origin of the optical anisotropic absorption was in the uniaxial orientation of nano-scale fibrils. This indicates that the oriented FTM films possess extremely large domains extended over 5 orders from micrometer to 10 centimeter scale. The findings represent that FTM is a simple and effective casting method to provide large-scale and uniform drop-cast films.

Key words: drop cast, π -conjugated polymer, polythiophene, polyfluorene, anisotropy

1. INTRODUCTION

Organic electronics are the next generation technology to replace conventional electronic devices into flexible and light-weight ones. Many researchers have been investigated and developed the practical use of organic-electronic devices in many fields.

π -conjugated polymers are expected to use in the organic electronic devices with these processability. Thanks to the validation of the repeating unit as the monomer synthesized with several π -conjugated elements via the recent coupling reaction technology, huge types of fusible polymer semiconductors can be developed and evaluated in their semiconductor functionality.

Since π -conjugated polymer being main chain structure, the transport characteristics are intrinsically anisotropic. It was reported that poly(3-hexylthiophene) (PHT) tends to form nano-scale fibrils by controlling the solution conditions.[1] Some researchers intentionally incorporate such fibril structure to practical electronic devices.[2] The aggregation state of macromolecules varies with the speed of volatilizing the solvent and freezing the conformation. Therefore, electronic characteristics of polymer semiconductors are sensitive to the morphology of the thin film. The casting methodology to prepare organic semiconductor film is the key technology to control of the distribution of anisotropy. The casting process play the important role of determining the device performance.[3]

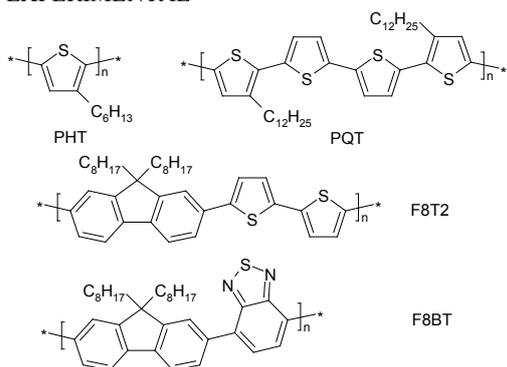
Many types of casting methodology have been developed to provide thin films of organic

semiconductors. Drop-cast is one of the ideal procedures to provide a film consisted with large coherent domains. However, the nucleation during volatilize the solvate formed multiple islands of clod during the solute started to solidify. Thus, the development of preparation method to obtain a uniform cast-film is strongly desired for educing the intrinsic transport performance.

We proposed the concept of "liquid substrate" for casting organic thin-film.[4] The film preparation procedure of processable materials temporary cast on a liquid substrate followed to transfer the device substrate after solidified on the liquid surface. Liquid substrate provides the mobile substrate on which the nuclears can join with each other. π - π stacking between multi-domains is also possible to fuse together. This method is so-called "Floating-film Transfer Method (FTM)". This method was found to involve several additional features such as to provide large-scale, anisotropic, and multiple layering functionalities.[5,6] The most key feature of FTM is arrowed to self-form thin cast-films by the aggregation of materials on liquid substrate. The dynamic casting mode of FTM provides a pressure or a tension force on the film during continuous solidifying, by which anisotropic characteristics could be incorporated in the film.[6]

This paper reports anisotropic characteristics of thin films consisted of polythiophene and polyfluorene derivatives prepared by FTM. Photonic characteristics and morphologies of these cast films are reported in order to discuss about the mechanism to generate the orientation in thin films.

2. EXPERIMENTAL



Chemical structures and abbreviations of π -conjugated polymers used in this study

All the polymer semiconductors were chemically synthesized according with the literatures. Regioregular poly(3-hexylthiophene) (PHT) was synthesized using Grignard metathesis.[7,8] 3,3'-didodecyl-quaterthiophene were synthesized with the modified turbo-Grignard magnesium reagent preparation.[9] Polymerization has been done with $FeCl_3$ as catalyst to obtain poly-quaterthiophene(PQT).[10,11] All the fluorene-based co-polymers were synthesized with Suzuki coupling.[12] All the polymers were purified by removing oligomers or low-coupling component with a Soxhlet extraction with acetone.[13]

Polymer semiconductor solution was prepared to dissolve polymer powders in dried chloroform. After polymer powder was mixed with solvent, filled with dry N_2 gas, warmed up over $100^\circ C$ and self-cooled to room temperature to use as the solution of polymer semiconductor. An optical transparent or quartz glass was used for photonic analysis. The surface was hydrated with APM method, followed by the silanization with octyltrichlorosilane in dry toluene as hydrophilic substrate.[14]

Two types of casting procedure were used for comparison. A mixture of ethylene glycol and glycerol was used for casting liquid substrate. In a petri dish having 10 cm long as diameter, around 50 μl of 0.5 wt% semiconductor solution was dropped on a center of the petri dish, by which the solution was gradually spread over the surface of the liquid. The chloroform was swiftly volatilized from the head of the solution with propagating and forming film outside the solution. The film was solidified to leave the film for 5 minutes completely to volatilize the solvent. A part of the floating-film was transferred on a hydrophilic substrate. Spin-coating films also prepared to spin at 3000-5000 rpm for 120 seconds for comparison.

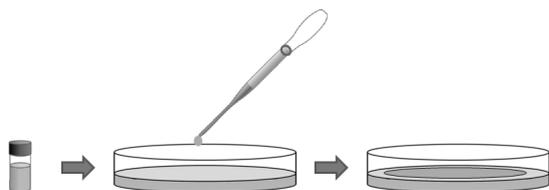


Figure 1: Schematic drawing of FTM procedure.

Optical measurements have been done with Jasco V-570 spectrophotometer for absorption spectra and Jasco FP-6500 for photoluminescence (PL) spectra. AFM images were obtained by JEOL SPM5200 with probes of Olympus OMCL-AC200TSC3.

3. RESULTS AND DISCUSSION

3.1 Polythiophene derivatives

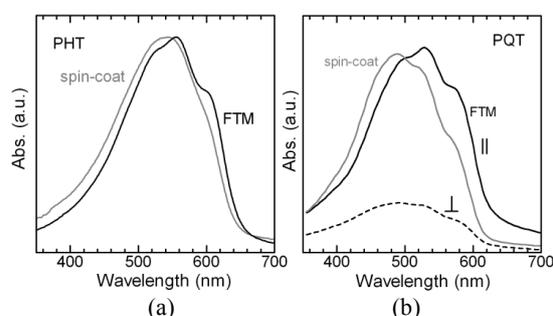


Figure 2: Comparison of absorption spectra of thin films prepared with FTM (black line) and spin-coating (gray line) of (a) PHT and (b) PQT through a polarizer, respectively.

Fig.2 (a) shows the comparison of absorption spectra with spin-coating and FTM films. As found, clear vibronic peaks at 525, 554 and 608 nm was appeared in the FTM film, which is unclear in the spin-coated one. The appearance of the vibronic peaks in the PHT film spectra represents the stretched conformation of many polythiophene main-chains into a similar manner. A well-growth of the low transition mode of 0-1 mode rather than that of 0-2 mode shows the stretched structure of main-chains.[4,15,16]

Fig.2 (b) shows the comparison of absorption spectra of PQT films. In the case of PQT, vibronic peaks were clearly located at 490, 526, and 576 nm for both spin-coating and FTM films. 0-2 mode of the vibronic peak was the maxima as similar to that in PHT and in perpendicular of FTM. In this case, clear anisotropic characteristics in absorption were revealed with 4.4 as dichroic ratio.

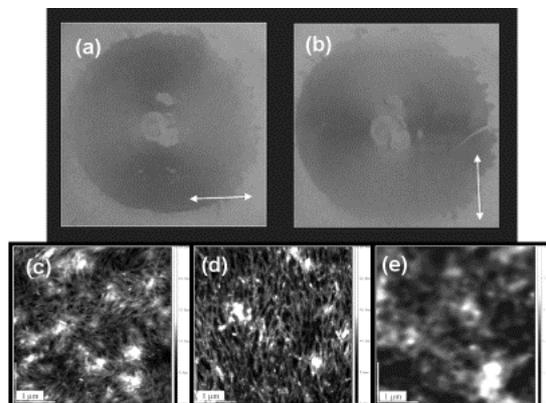


Figure 3: (a), (b): Polarized optical images of a PQT film floated in a petri dish (white arrow as the polarized axis). AFM images of (c):spin-coating film, (d):FTM at $20^\circ C$, and (e):FTM at $60^\circ C$, respectively.

It should be noted that in the FTM film, whole the circular thin-film formed into concentric orientation as could be seen through a polarizer. Such anisotropic domain could not found in PHT films. PQT is well-known to show a clear thermotropic liquid-crystal (LC) transition at around 150 °C. In the case in PHT, some documents reported a kind of LC phase transition at high temperature around 200 °C.[17] The comparison of the difference of these thermal characteristics suggests that PQT rather possesses clear thermotropic LC phase possibly thanks to the mesogen unit of bithiophene in the repeating unit. These characteristics might show the different results in the orientation characteristics in FTM procedure.

Upper panel in Fig. 3 shows the optical images of a PQT film floated on ethylene glycol/glycerol liquid substrate in a petri dish. Lower panel in Fig.3 shows AFM images of oriented PQT film. The uniaxial alignment of nano-scale fibrils was found along with the optical orientation in FTM films prepared at room temperature. In the case in spin-coating films, the fibrils lie randomly to all the directions. As shown in Fig. 2, both in spin-coating and FTM films possesses the vibronic structure. Thus, the vibronic mode in the PQT film is possibly attributed to the fibril formation. The consistent alignments of anisotropy in both the optical images and the AFM images support that the anisotropic absorption is attributed to the oriented fibrils.

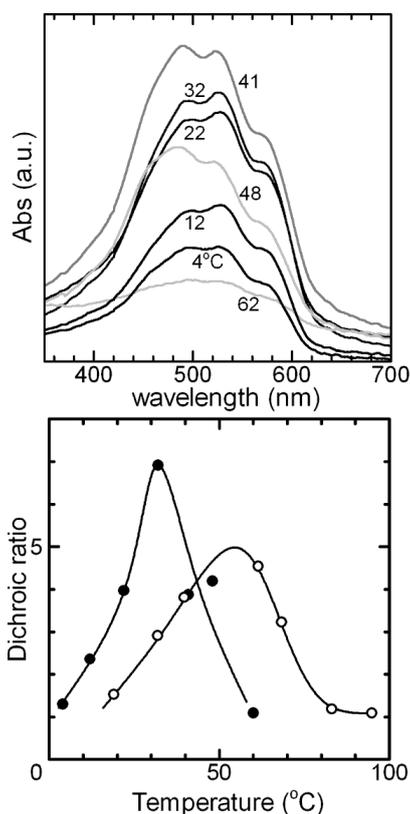


Figure 4: (a):Parallel-polarized absorption spectra of oriented PQT films prepared by FTM at various temperature and (b):temperature dependence of dichroic ratio of the absorption peak at 526 nm.

As found in the optical images shown in Fig. 3, whole the 7 cm diameter film was uni-oriented into concentric fashion, indicating that the oriented domain size is over centimeter scale. It should be noted that the size of fibrils are a few μm in length, whose alignment was expanded near 10 cm. This indicates that the uniform orientation of FTM was spread over 5 orders of magnitude. This indicates that FTM is one of the ways easily to fabricate extremely large oriented-domains.

Figure 4 (a) shows the comparison of parallel polarized absorption spectra of PQT cast at various temperatures. As could be found, up to 40 °C, 0-1 mode vibronic peak at 526 nm was the maxima. The maximum peak was shift to the 0-2 mode vibronic peak at 490 nm was dominant beyond the temperature over 40 °C. The peak shift is corresponding to the spectra in spin-coated film. The loose packing of polymer chains due to the preparation at high temperature might occur likely into one in spin-coated film. As shown in Fig.3 (c), the fibril structure was disappeared when prepared at 60 °C. The spectral shape was also drastically changed, correspondingly. These results also support that the vibronic peaks could be attributed to the electronic structure in the fibril.

The intensity of absorption varies with the preparation temperature. The peak-height of the spectra coarsely represents the thickness of the film. Two factors, namely, the volatile speed of solvent and the propagation speed of solutions, control the film thickness. The balance of both speeds will provide the maximum orientation. The volatilzability of solutions and the viscosity of liquid substrate are, therefore, the important factors to determine the film characteristics.

In order to investigate the effect of molecular weight on the orientation procedure of FTM film, high-molecular powder was prepared by the Soxhlet extraction with CH_2Cl_2 to remove relative low-molecule component[13] and prepared high-molecular PQT solutions (High-PQT). Although concentrically oriented FTM films could be obtained when to use High-PQT solutions, the shape of FTM film floated on liquid substrate was branched off like in a starfish structure.[5] Lower panel in Fig. 4 shows the temperature dependence of dichroic ratio of the oriented FTM films prepared with both whole-PQT and High-PQT solutions. As can be found, the orientation peak-temperature was shift higher zone in the High-PQT. In common, low-molecular weight component is well-dissolved in a solvent. Thus the fibrils consisted with low-molecular polymers are also easily dissolved even at near the room temperature preparation. Besides this, the dissolving temperature of the fibrils with high-molecular polymers should be higher. The finding temperature shift of the maximum dichroic ratio as shown in Fig. 4 (b) is well-corresponding to the temperature dependence of solubility. It is interesting to note that the starfish like structure was changed into round shape if a small portion of fluidic paraffin was added in the High-PQT solution. This suggests that the low-molecular component of PQT plays a role of plasticizer for form round shape FTM film.

3.2 Polyfluorene copolymers

Figure 5 shows the polarized absorption and PL spectra of two types of co-polymers based on fluorene. As shown here, both types of the fluorene-based copolymers also show the orientation with FTM process. For F8T2, the maximum peak was located at the most long wavelength of 489 nm, which was shift to 460 nm in perpendicular one. The dichroic ratio at this peak is 1.9. In the case in PL spectra, a relative high dichroic ratio of 3.9 was obtained. For F8BT, a similar peak shift was also observed in absorption spectra with dichroic ratio of 1.9, which was 3.0 in PL spectra. These characteristics are quite similar with each other and with those of poly(9,9'-dioctylfluorene) as reported in the literature.[6] Namely, the orientation characteristics in FTM procedure are reproducible and well reflect the polymer characteristics. It is well known the existence of thermotropic LC characteristics in polyfluorene-based copolymers, also. These are possibly contributed even in this FTM procedure.

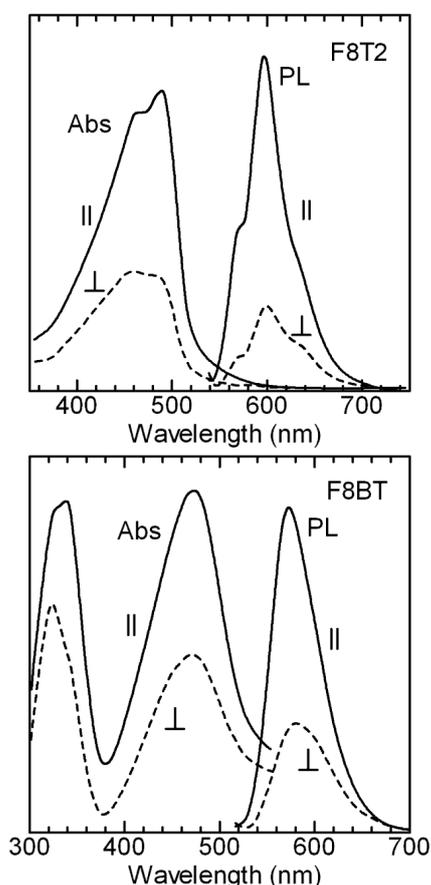


Figure 5: Polarized absorption and PL spectra of the fluorene based copolymer of (a)F8T2 and (b)F8BT prepared with FTM. Solid and dashed lines represent parallel and perpendicular spectra through a polarizer, respectively.

The FTM procedure reported in this study and in the literature[4-6] is to be categorized as the dynamic FTM in terms of the concentric process of solution with the volatilization during the solution spreading. In this procedure, it is possible to generate some lyotropic LC phase transition at a certain high-concentration state due

to their intrinsic LC characteristics.[18-20] A sort of self-organization force in the materials may also assist to generate the anisotropic domain formation in FTM.

3. SUMMARY

Large-scale drop-cast films of π -conjugated polymers could be obtained with Floating-film transfer method (FTM). Optical and topographic characterization revealed that the obtained uniform orientation in some FTM films should be attributed to uniaxial alignment of nanofibers probably thanks to the intrinsic liquid-crystal characteristics of these π -conjugated polymers.

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