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Orientation Characteristics of Non-regiocontrolled Poly(3-hexyl-thiophene) Film by FTM on Various Liquid Substrates

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Abstract. Orientation characteristics of non-regiocontrolled poly(3-hexylthiophene) (NR-P3HT) films prepared by dynamic casting of floating film and transferring method (FTM) has been investigated. The film was first cast on liquid-substrate to obtain as a floating-film followed by its transfer on solid-substrate such as white-glass or Si-wafer in order to evaluate their optoelectronic characteristics. As a possible key-factor to generate the orientation of conjugated polymer in this method we focused on the components of liquid-substrate in this study. The orientation dependence upon various liquid-substrates reveals that dichroic ratio strongly changes with liquid-substrates. Pictures of floating-film show the change in size of floating-parts depending upon the liquid-substrate, representing the expansion length of casting solution upon the viscosity. These findings have indicated that spreading speed of polymer solution and solvent evaporation speed controls the size of floating-film leading to change in the orientation intensity. The multilayer coatings of oriented NR-P3HT films were used for polarized FTIR analysis exhibiting clear dichroism. The obtained dichroic characteristics were well corresponded with in-plane, out-of-plane and non-oriented vibronic modes of P3HT.

1. Introduction

Solution processing is one of the important key-features to prepare organic electronic devices with ease and at larger scales. Such processing feature in organic electronics contributes not only to be cost-effective but also the energy efficient process which is advantageous over the Si-based electronics. However, the organic-semiconductor films prepared with solution process exhibits varied film morphologies due to random mixing and/or alignment of molecules during solid phase condensation. The electronic characteristics like carrier transport drastically changes with the film morphology. Casting procedure to prepare the organic-semiconductor film, therefore, is the most important key-factor to bring out the potential performance of these materials. Origin of this varied film morphology is associated with the intrinsic anisotropy of organic semiconductors in terms of their geometric and electronic structures. Many efforts have been paid to obtain the molecular alignment in casting process in order to control the film morphology. In particular, conjugated polymer (CP) is the most anisotropic organic semiconductor. Thus, the orientation methodology of CP with facile and rapid way is strongly desired in order to deploy the profit of its anisotropy. We have developed a novel casting procedure to

promote the orientation of CPs on liquid-substrate, which can be expressed as dynamic casting of floating-film and transferring method (dynamic FTM) [1]. Importance of this procedure lies in the utilization liquid-substrate for casting of a thin film. Liquid-substrate provides the mobile surface to combine under solidifying parts with each other leading to the formation a uniform film. In particular, if we choose a volatile solvent such as chloroform for casing solution, the floating-film solidification occurs immediately during spreading of the solution on liquid-substrate. In this case, floating-film formed under solidification with spreading, leading to compress the film with the motion of liquid-substrate resulting in to an oriented floating-film. This method is quite unique and quick to deposit a centimeter scale of oriented film and it can be coated on various organic surfaces without having interlayer interferences.

Various factors such as volatile speed of solvent, spreading speed of solution, solidification speed of materials will affect on the orientation characteristics in dynamic FTM. In fact, volatile solvents such as tetrahydrofuran and dichloromethane can provide similar oriented films by dynamic FTM at room temperature. Against this, benzene-based solvents such as toluene and chlorobenzene failed to provide oriented floating-film in the same condition. The orientation characteristics vary with the liquid-substrate and the casting temperature, also. Considering these complicated states for obtaining the well-orientated films in dynamic FTM, it is important to proceed the step by step analysis of each casting factor on the orientation characteristics, carefully.

Poly(3-hexylthiophene) (P3HT) is one of the most investigated conjugated polymers pertaining to its semiconductor characteristics. Since the discovery of controlled synthetic method of P3HT to react selectively in the head-to-tail manner via a modified Kumada-Tamao-Corriu cross-coupling [2] with Ni catalyst [3], drastic improvements of transport characteristics have been realized leading to high performance electronic devices such as organic solar-cells [4] and organic thin-film transistors (OTFTs) [5]. Non-regiocontrolled P3HT (NR-P3HT) synthesized with oxidative polymerization using FeCl3 [6, 7], therefore, rather reduced to be investigated as a classical material. NR-P3HT, however, still possesses advantages to polymerize using cheap raw materials with relatively simple methodology and high yield. Recently, we have found that NR-P3HT could be oriented with high dichroic ratio (DR) of 9.3 via dynamic FTM. NR-P3HT is, therefore, regarded as a proper target material for the research of orientation characteristics with dynamic FTM. In this work, we have focused the effect of liquid-substrate on the orientation characteristics in dynamic FTM. For the purpose to vary the viscosity, we choose several mixtures of distilled water (Wt) and ethylene glycol (Eg) as low-viscosity and mixtures of Eg and glycerol (Gl) as high-viscosity liquid-substrates. Orientation characteristics of NR-P3HT films thus prepared have also been clarified by polarized optical measurements.

2. Materials and Methods

NR-P3HT has been oxidative synthesized with $FeCl_3$ catalyst. The detail procedure of polymerization is as follows. 3-hexylthiophene/$CHCl_3$ solution was dropped in $FeCl_3$/$CHCl_3$ slurry at -5°C with stirring. The final ratio of 3-hexylthiophene:$FeCl_3$ in the mixture was set at 1:4. This mixture was reacted with stirring at -5°C for overnight (~12 hs), then quenched with 1M HCl to stop the reaction. The solid part was collected and dissolved in fresh $CHCl_3$. This solution was mixed with NH_4OH aqueous solution. The mixture was vigorously stirred with boiling, then separated aqueous part and added a fresh NH_4OH solution, again. This procedure was repeated for 4 times. After that, the $CHCl_3$ solution was separated and added 0.05M of ethylenediaminetetraacetic acid (EDTA) aqueous solution to remove Iron-based impurities [8]. This mixture was stirred with warming for 1h for purification, repeatedly. The dark orange $CHCl_3$ part was separated, washed with water, then filtrated to remove insoluble part. The fine $CHCl_3$ solution was condensed and precipitated in methanol. Again the obtained solid part was dissolved $CHCl_3$, then precipitated in acetone. The solid part was collected and washed by Soxhlet extraction with hexane in order to separate relatively low-molecular parts [9]. Finally, relative high-molecular NR-P3HT was obtained as dark brown powder. Regioregularity was confirmed to be about 80% by the area ratio of ^{1}H-NMR spectrum peaks at 2.56 (head-to-head coupling) and 2.80 (head-to-tail coupling) ppm as shown in figure 1.
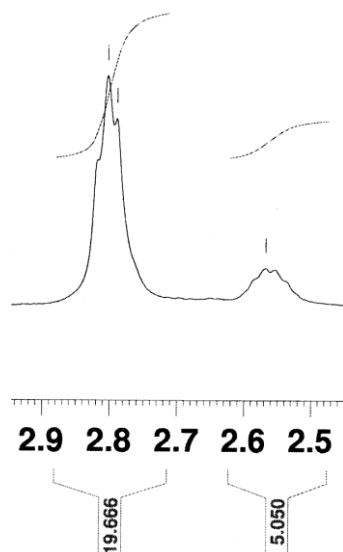
Figure 1. ^{1}H-NMR spectrum at α-methylene region. Area of the peaks are 19.666 at 2.80 ppm (head-to-tail coupling) and 5.050 at 2.56 ppm (head-to-head coupling) regions. This provides 79.6 % as the head-to-tail coupling ratio (regioregularity) of this NR-P3HT.

10 mg of NR-P3HT was typically dissolved in 1g of dehydrated chloroform to obtain 1% (in w/w) solution which was then used to cast thin film by dynamic FTM. Dynamic FTM was conducted by putting a droplet (about 10uL) of solution at the center of the liquid-substrate. The droplet quickly started to spread in all the direction and to solidify as a floating-film, simultaneously. After solidification the floating-film was left for several minutes in order to complete the evaporation of solvent (chloroform). A solid-substrate such as Si-wafer and/or white-glass was put on an oriented part of the floating-film to transfer it on the substrate. The surface of the transferred floating-film was washed with methanol and dried by blowing air to remove dews remaining on the surface. The coated film can be easily confirmed by the naked eyes owing to change in color as compared to non-coated surface.

A single layer of FTM coating provides oriented films of NR-P3HT having the thickness of about 20 nm measured by interference microscopy Nikon Eclipse LV 150. Multiple coatings of oriented NR-P3HT have also been done in order to increase the thickness for spectroscopic characterization. Finally, we could obtain about a 800 nm-thick oriented film by the multiple-coatings. For the purpose to investigate the effect of liquid-substrate viscosity on orientation, a variety of binary mixture of water and ethylene glycol (Wt/Eg) or ethylene glycol and glycerol (Eg/Gl) were used as liquid-substrates. Optical dichroic characteristics were investigated by the polarized absorption spectra obtained through a Glan-Thompson prism with JASCO (V-570) spectrophotometer. Polarized FTIR spectra were also measured by JASCO Fourier transform infra-red spectrometer (FTIR-4100) through polarizer unit. We used DR as the relative height of peak absorption in both the parallel- and orthogonal-spectra at the peak wavelength in the parallel-spectra in this study.

3. Results and Discussion

Figure 2 shows the photographic images for the floating-film deposited on 7 cm-diameter liquid-substrate. It can be seen from figure 2 that size of inner thick and non-uniform part reduces with increasing the viscosity of the liquid-substrate. This suggests that viscosity of liquid-substrate strongly affects the molecular condensation of floating-film during dynamic FTM.
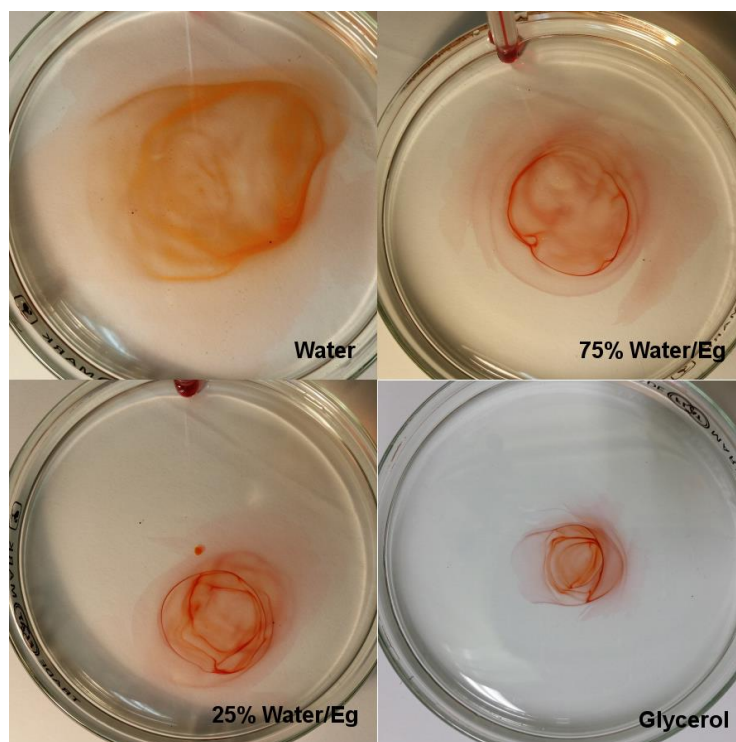
Figure 2. Pictures of floating-film cast in a petri-dish having 7 cm-diameter.

A perusal of thin film formation under dynamic FTM reveals that it is consisted of the three-type parts. The outer (initially formed) dispersive part seems to be very thin (sometimes invisible). The middle one shows fine orientation with good uniformity in thickness. The final inner (central) part, deposited with middle part in continuation is although good in the orientation but with least uniformity. Both of the outer and the middle parts are solidified from the outer to the inner direction. Against this, at the end of solidification the central area filled by remaining solution solidifies from the outer to the center area. The procedure to form the inner part is quite similar to the solidification of drop-cast film on the solid-substrate. The change in the solidification from outer to the inner direction for inner parts suggest that the remaining solution cannot be spread any more, then forms a film with evaporation of solvent, under limiting the motion of solution at remaining narrow area. The immobile characteristics of solution for solidification of the inner parts do not match to the concept for liquid-substrate. Therefore, the most featured part as dynamic FTM is the oriented middle part in floating-film. Therefore, we selected to transfer the middle part of floating-film on solid-substrate as the well-oriented and uniform film for further characterization.

Various binary liquid-substrates were used for obtaining the oriented films. DR obtained by polarized-absorption spectra as shown in the insets in figure 3 depicts the viscosity dependent DR. Viscosities of the liquid substrates used in this work were varied by mixing ratio of water/ethylene glycol (Wt/Eg) or ethylene glycol/glycerol (Gl/Eg). This figure clearly illustrates that the orientation intensity (indexed by DR) strongly depends upon the liquid-substrate. It should be noted that the viscosities of Wt, Eg and Gl were 1, 16 and 1420 mPa.s, respectively. The viscosity of liquid-substrate controls the spreading speed of polymer solution. Therefore, finally inverse of x-axis in figure 3 can be regarded as the spreading speed. By considering the images of floating-film shown in figure 2 along with figure 3 the size of inner part reduces with increasing the spreading speed. These results suggest a detailed mechanism to generate inner part after solidification. Increase in the spreading speed leads to the enhanced coverage area by the outer and the middle parts also. The central part not to be covered by the outer and the middle parts, therefore, reduces in size, which defines the size of the inner parts. This finding of DR dependence on viscosity as discussed above indicates that a sort of optimal

matching for both of the spreading speed of solution and the evaporation speed of solvent is expected to promote the orientation of NR-P3HT.
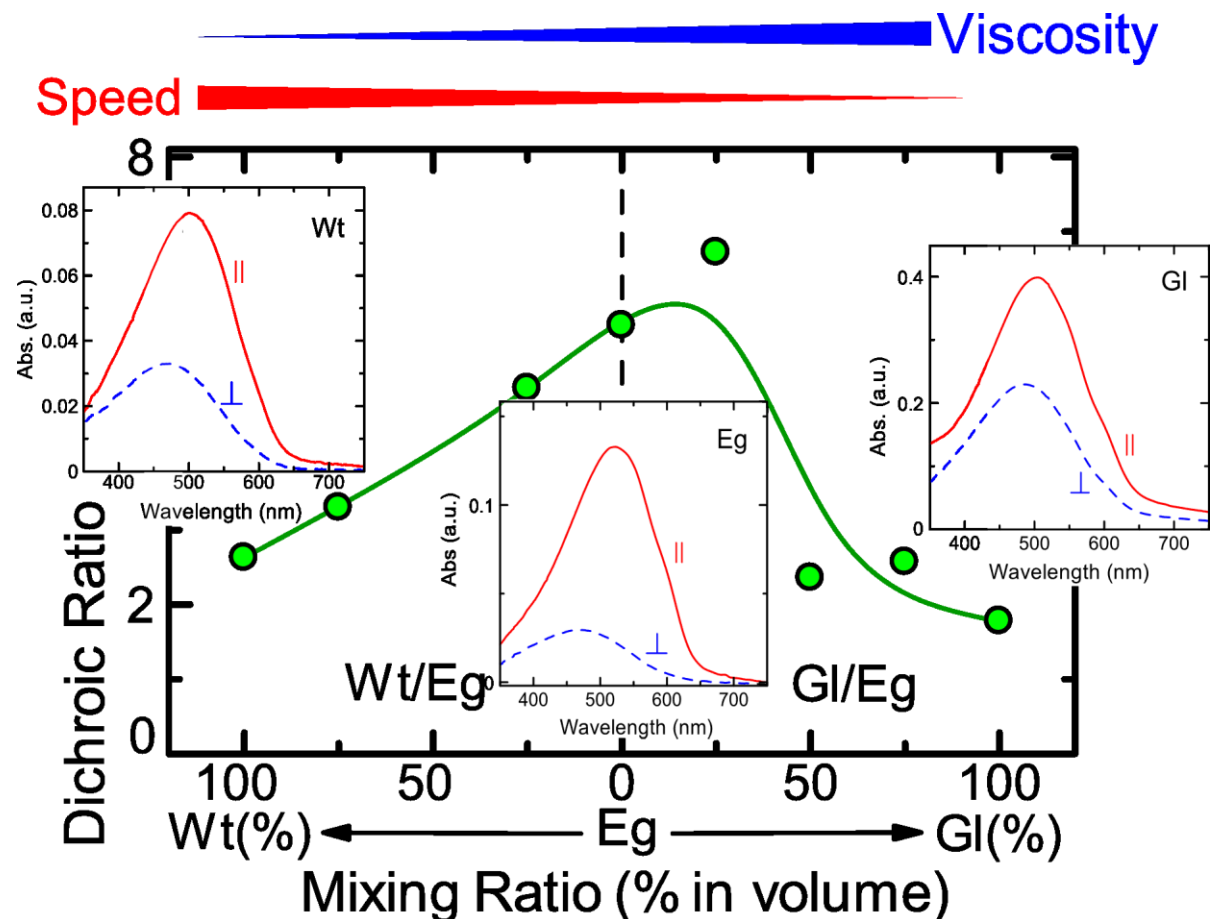

Figure 3. DR as a function of mixing ratio in various binary liquid-substrates. Insets show the polarized absorption spectra of NR-P3HT films cast on Wt, Eg and Gl liquids.
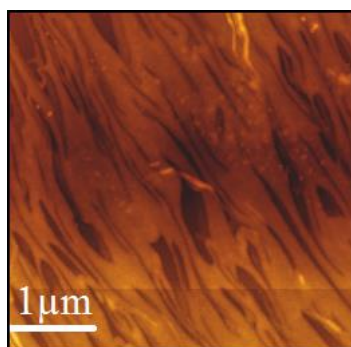

Figure 4. AFM image of oriented NR-P3HT film surface.

Figure 4 shows an AFM image of oriented NR-P3HT film surface. As can be found, NR-P3HT film is consisted of uniaxially-stretched domains. This direction is matched to the parallel direction of the polarized absorption spectra (shown in the insets in figure 3). This indicates that the macromolecules of NR-P3HT lie into the same direction in these stretched domains.

Figure 5 shows the distinctive vibration band of polarized FTIR spectra of an oriented NR-P3HT film. Thanks to the thickness (about 800 nm) prepared by multi-coating with FTM, relatively high-absorptions could be obtained at 1456, 1506 and 1517 cm^{-1} in parallel FTIR spectra. These bands are assigned as the in-plane vibration modes of thiophene ring [10]. Against this, a clear inverse dichroism was found at 825 cm^{-1} with a new band at 835 cm^{-1}. These dual peaks has been assigned as the out-of-plane mode of thiophene ring [10, 11]. Contrary to these bands, non-dichroic absorptions were found at 722 and 1377 cm^{-1}, which are assigned as vibration modes of alkyl side chain of the thiophene substituent. It should be noted that the wide-band area at around 1420-1490 cm^{-1} is known to be consisted of the overlapping both of the thiophene-based in-plane and alky modes [11, 12]. A careful perusal reveals that the band at 1464 cm^{-1} is non-dichroic and the three-peaks at 1419, 1439 and 1456 cm^{-1} shows clear dichroism. In particular, the dichroic ratio at 1419 and 1439 cm^{-1} seems to be similar as those at 1506 and 1517 cm^{-1}. It is also reported that there are three in-plane modes at around 1417-1460 cm^{-1} [11]. These results support that the peaks at 1419 and 1439 as well as 1456 cm^{-1} can be assigned as the in-plane vibration modes of thiophene ring, and 1464 cm^{-1} is belong to alkyl modes, respectively. The finding separable assignments at this complex band can be easily carried out owing to the uniform strong orientation in this thick film.
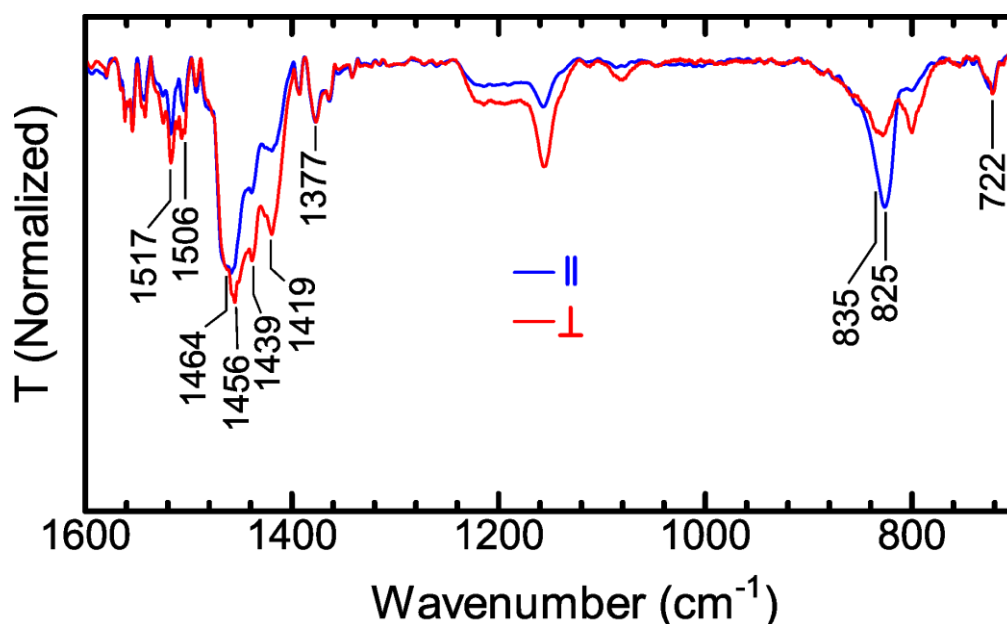

Figure 5. Polazied FTIR spectra of a muli-layerd NR-P3HT film prepared by dynamic FTM.

4. Conclusions

Various binary liquid-substrates were used for obtaining oriented films of NR-P3HT. A correlation between the spreading speed of solution and the solidification speed of floating-film is found to be an important factor to identify the orientation intensity for dynamic FTM. Thanks to the macroscopic multiple parallel-coatings of oriented NR-P3HT by dynamic FTM, various polarized spectroscopic characterization can be easily carried out to various thick oriented films with a simple polarizer.

Acknowledgments

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