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Casting Control of Floating-films into Ribbon-shape Structure by modified Dynamic FTM

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Abstract. We have developed a new method to obtain Ribbon-shaped floating films via dynamic casting of floating-film and transfer method (dynamic-FTM). Dynamic-FTM is a unique method to prepare oriented thin-film of conjugated polymers (CPs) which is quick and easy. This method has several advantages as compared to the other conventional casting procedure to prepare oriented CP films. In the conventional dynamic FTM appearance of large scale circular orientation poses difficulty not only for practical applications but also hinders the detailed analysis of the orientation mechanism. In this present work, pros and cons of this newly proposed ribbon-shaped floating-film have been discussed in detail from those of the conventional floating-film prepared by dynamic-FTM.

1. Introduction

Conjugated polymers (CPs) have captivated a lot of attentions in the recent past for their potential applications in organic field effect transistors (OFETs), light emitting diodes (LEDs) and photovoltaics. The solution processing capability of CPs is one of the important features rendering their suitability towards potential application in the area of plastic electronics owing to the cost effective process for fabrication of thin films. Thin film morphology of the CPs plays a dominant role in deciding the charge transport properties, which arises from the self-assembly promoted aggregation of macromolecules while solid phase condensation. Casting procedures to prepare semiconducting layer with CPs is, therefore, an important and decisive step to characterize the transport performance. Although spin-coating is one of the most widely used techniques for fabricating thin films, the random spatial arrangement of main-polymeric chains limits its usage for fabricating high performance organic electronic devices [1]. One of the amicable solutions for this problem is the introduction of macromolecular alignment of CPs. Various methods to prepare oriented thin-films such as friction transfer method [2], mechanical rubbing [3], solution flow [4], capillary action [5], solution shearing [6], slide coating [7] and strain alignment [8] etc. have been developed and investigated in-detail towards the analysis of their orientation characteristics. Although these techniques have demonstrated a potential importance for fabricating organic electronic devices by using oriented thin films of CPs in the last one decade, important challenges like simplicity of fabrication process and preparation of multilayer oriented films are yet to be taken into consideration.

We have developed a dynamic casting of thin floating-film of CPs on liquid-substrate followed by its transfer on a desired substrate which has been named as dynamic-FTM. This is a simple, cheap and quick casting method to provide oriented films of CPs. The oriented area reaches up to centimeter-scale which enables us to construct multilayered thin-films with the preserved oriented morphology [9-11]. However, remaining obstacles like non-uniformity in thickness and control of orientation direction are still remaining challenges which have to be solved. In order to resolve these problems, we have developed a new casting method by modifying the casting of floating films into the ribbon-shape by introducing a custom-made slider to control the spreading of the oriented films. In this study, we have compared the film characteristics prepared by this ribbon-shaped dynamic-FTM and conventional dynamic-FTM. Role of individual casting parameters such as solution concentration, viscosity of liquid-substrate and casting temperature have been investigated by polarized electronic absorption spectroscopy.

2. Experimental

Non-regiocontrolled poly (3-hexyltiophene) (NR-P3HT) was selected as the representative polymeric material in this study. It has been synthesized by chemical oxidative polymerization using $FeCl_3$ catalyst and purified as per our earlier publication [15]. The regioregularity (head-to-tail coupling content) was confirmed to be about 80 % by proton nuclear magnetic resonance investigations. Dehydrated chloroform, purchased from Wako Chemicals, was used for the thin film casting. Synthesized NR-P3HT was highly soluble in the dehydrated chloroform and used to prepare two types of solutions, 1% and 2% (wt/wt). Procedure to cast the ribbon shaped floating-film has been schematically shown in the Fig. 1. Hydrophilic liquid mixture was first made and poured into a rectangular tray which serves the purpose of liquid-substrate. A hand-made slider made of PTFE was put near the one of edges in the tray. About 15 µl of NR-P3HT solution in chloroform was dropped to the slider. When the droplet reached to the slider/liquid-substrate boundary, there was a quick and unidirectional spreading of the solution followed by continuous solidification leading to the fabrication of ribbon-shaped floating-film. After this casting, the obtained floating-film was left for 10 minutes to ensure complete evaporation of the solvent. Since the orientation of CP in the floating-film was of macroscopic in order, it was easily confirmed through a linearly polarized film with the naked eyes.

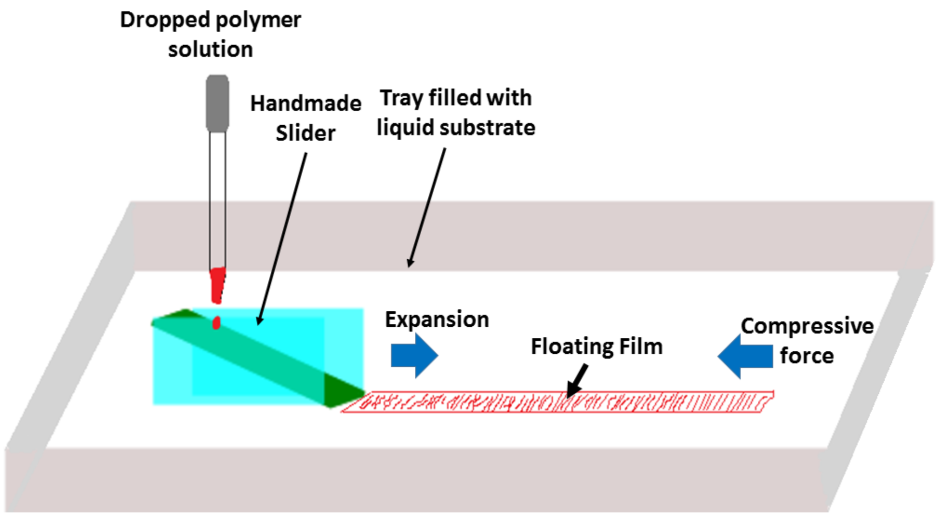

Figure 1. Schematic representation of the set-up for casting ribbon-shaped floating-film

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The resulted floating film was stamped on transparent solid-substrates for the orientation analysis. The surface of the solid substrates were treated with hexamethyldisilazane (HMDS) to increase the hydrophobicity in order to ensure easy and better adhesion of the thin floating-films during stamping. The transferred film surface was washed with methanol in order to remove any remaining liquid substrate on the stamped surface followed by drying. In order to investigate the effect of liquid-substrate viscosity on the molecular orientation, a variety of binary solvent mixtures like water and ethylene glycol (Wt/Eg) or ethylene glycol and glycerol (Eg/Gl) were used to prepare the liquid-substrates as per our earlier publications 14,15]. Optical anisotropy in the oriented thin films was investigated by the polarized electronic absorption spectra obtained through a Glan-Thompson prism with JASCO V-570 spectrophotometer. The orientation intensity of the NR-P3HT in these films was calculated from polarized absorption spectra as the optical dichroic ratio (DR).

3. Results and Discussion

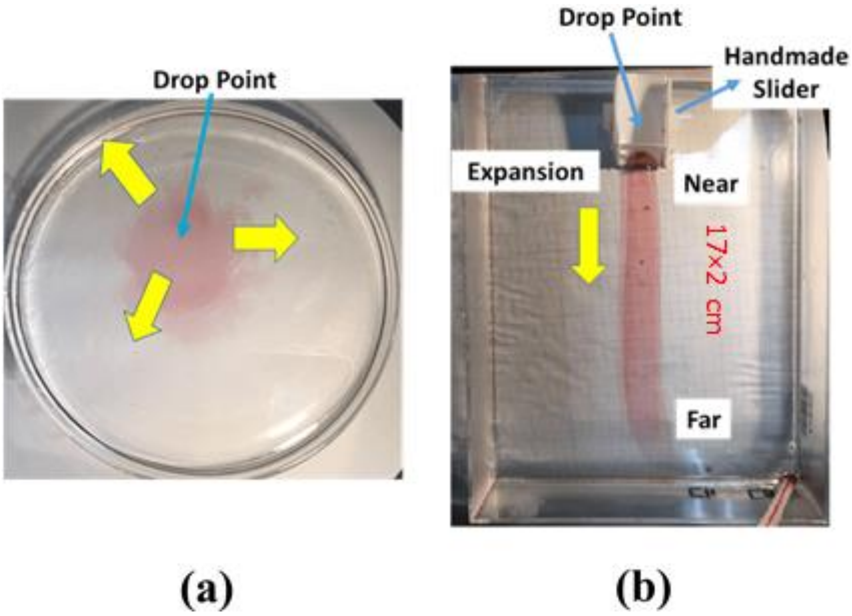

Figure 2. Optical photographs of casting with (a) conventional dynamic FTM and (b) Ribbon-shape FTM procedure, respectively.

Figure 2 shows the photographic images of the obtained floating-films prepared by the conventional and Ribbon-shaped FTM methods, respectively. It is clearly observed that the obtained shape of the floating-film drastically changes depending on the employed method of the film casting under dynamic FTM. A circular floating-film with some dispersive parts formed in the floating film can be clearly seen for the thin film fabrication using conventional dynamic-FTM. On the other hand, this newly introduced slider changed the shape of the floating-film into the Ribbon-shaped one. It is obvious that the later method has advantages in terms of detailed analysis as well as for the easy handling the transfer process due to its large scale rectangular shape. Polarized electronic absorption spectra of Ribbon-shaped floating-film casted on glass substrate has been shown in the Fig.3. A non-polarized electronic absorption spectra of a spin-coated NR-P3HT film has been also incorporated in order to compare the orientation behavior. DR of the Ribbon-shaped floating-films was found to be 2.4. It can be easily seen that absorption maximum (λ_{max}) in the electronic absorption spectrum of parallel oriented NR-P3HT film was located at 505 nm along with the presence of vibronic shoulders. Interestingly, λ_{max} in the electronic absorption spectrum of spin-coated film was found to be at 498 nm with a clear red shift of 7 nm in the Ribbon-shaped FTM film. Vibronic shoulders around 540 nm and 602 were appeared in the similar manner to that observed for the conventional dynamic-FTM.

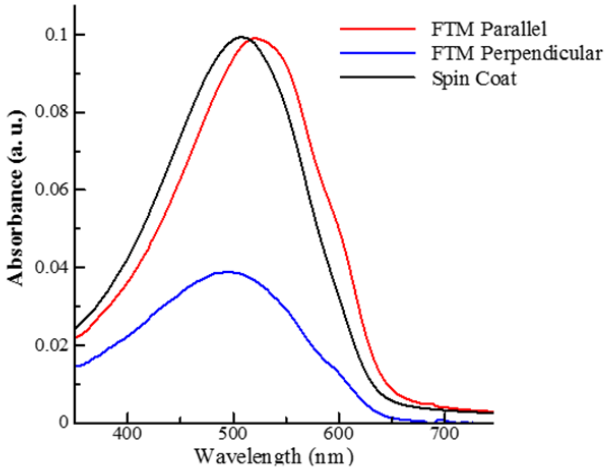

Figure 3. Polarized electronic absorption spectra of NR-P3HT thin films prepared by spin coating and Ribbon-shape FTM

These findings represent the presence of the increased π-orbital delocalization on main-chain [16]. The results support that the films fabricated by this newly developed method also have enhanced π-stacking and such films are suitable for the fabrication of optoelectronic devices. A relatively small DR of 2.4 observed in this ribbon-shaped oriented film indicates that developed slider method provides a weak orientation as compared to that of the conventional dynamic-FTM. A clear reason for this cannot be assigned at the present stage but further development and optimization of the slider shape is required for achieving the high orientation. Although the orientation intensity is small in the ribbon-shaped films, it is worthy to note that λ_{max} is clearly red-shifted even in NR-P3HT as discussed above. It has been already demonstrated, that thin film casted via dynamic-FTM is found to show high transport performance as compared to that of the spin-coat film [12]. In addition, the orientation size can be reached up to several centimeter-scales and better than the conventional dynamic-FTM.

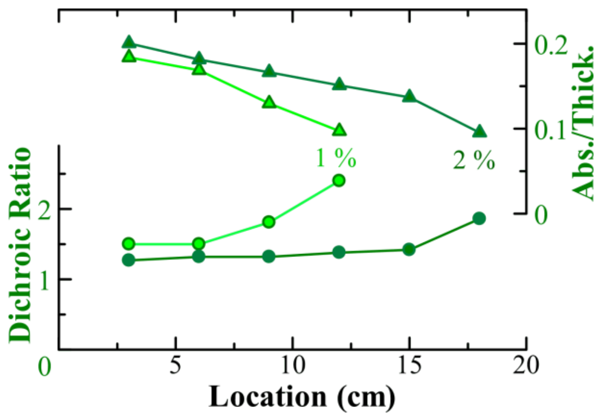

Figure 4. Variation of DR and peak absorbance with respect to the casting point (near). Variation in peak absorbance represents that the thickness of the film is less in the far region and higher towards the beginning (slider).

Figure 4 shows the location dependence of DR as well as the absorbance at the λ_{max}. Absorbance at λ_{max} at different locations of the ribbon-shaped FTM was also measured in order to investigate variation in thickness of the films. It is important to note that thin films casted towards the slider end in the Ribbon-shaped FTM exhibit nearly no change in the measured DR values up to >10 cm. This indicates that the

Ribbon-shaped casting method provides relatively uniform orientation especially towards the slider side. The film thickness tends to be thinner as a function of increasing distance of the casted film from slider side to opposite end. These location dependences were also observed even after changing the concentration of the polymer solution. Such information about the distribution of large-scale orientation is highly desired for the in-depth discussion about the orientation mechanism. In this context, Ribbon-shaped thin film casting procedure proposed here provides the considerable knowledge of orientation characteristics by dynamic-FTM. It is interesting to note that there is appreciable enhancement in the observed DR at the far area in the Ribbon-shaped floating-film. This could be explained considering the fact that at the initial stage of solidification of floating film, extent of molecular orientation is less due to the fast solvent evaporation and dragging viscous force from the liquid substrate. There is induction of molecular orientation is the result of competition between the film spreading and opposing viscous force posed by the liquid substrate which continues further with the advancing floating film.

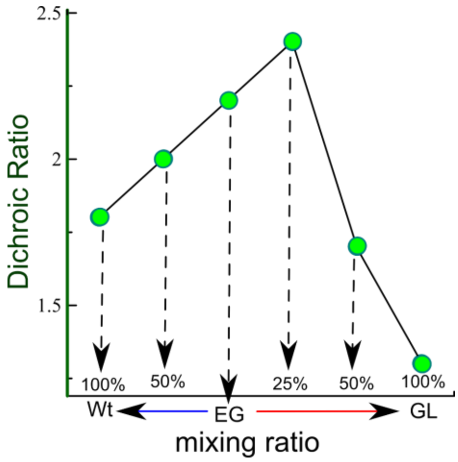

Figure 5. DR dependence on the binary liquid mixture of water, EG or GL as casting liquid-substrate

Figure 5 depicts the liquid substrate viscosity dependence of observed DR in the Ribbon-shaped floating-film where the viscosity was controlled by mixing the two miscible hydrophilic solvents of varying viscosities. All of the DR plotted here are taken at the farthest position giving the best orientation. Although DR is small as mentioned above, the orientation characteristics are quite the same of the floating-films obtained by the conventional dynamic-FTM as reported previously [14]. This fact also indicates that even by changing floating film fabrication method as mentioned above with Fig.2, the essential orientation characteristics remain well conserved. This is also very important to note that the Ribbon-shaped dynamic-FTM is useful for investigating the mechanism with various casting factors aiming towards the attainment of high molecular orientation. The proposed Ribbon-shaped dynamic-FTM is utilized for researching the orientation mechanism in dynamic-FTM and for optimizing the orientation condition towards the practical use.

4. Conclusions

We have developed a modified dynamic-FTM to obtain Ribbon-shaped floating-films. The resulting floating-films were confirmed to be oriented to perpendicular direction with respect to the propagation direction of the floating film. The orientation intensity given by the dichroic ratio (DR) was 2.4, which was relatively small as compared to the conventional dynamic-FTM. DR dependences on the distance from the dropping point, solution concentration and liquid-substrate were investigated as a preliminary investigation. These results exhibit almost the same characteristics as compared that observed in conventional dynamic FTM. The developed casting way can be utilized for investigating the orientation mechanism as well as for the optimizing the casting condition in dynamic-FTM.

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References

[1] Strawhecker K E, Kumar S K, Douglas J F and Karim A 2001 *Macromolecules* **34** 4669–72
[2] Nagamatsu S, Takashima W, Kaneto K, Yoshida Y, Tanigaki N, Yase K and Omote K 2003 *Macromolecules* **36** 5252–7
[3] Hartmann L, Tremel K, Uttiya S, Crossland E, Ludwigs S, Kayunkid N, Vergnat C and Brinkmann M 2011 *Adv. Funct. Mater*. **21** 4047–57
[4] Yamasaki N, Miyake Y, Yoshida H, Fujii A and Ozaki M 2011 *Jpn. J. Appl. Phys.* **50**
[5] Higashi T, Yamasaki N, Utsumi H, Yoshida H, Fujii A and Ozaki M 2011 *Appl. Phys. Express* **4** 91602
[6] Giri G, Delongchamp D M, Reinspach J, Fischer D A, Richter L J, Xu J, Benight S, Ayzner A, He M, Fang L, Xue G, Toney M F and Bao Z 2015 *Chem. Mater*. **27** 2350–9
[7] Karakawa M, Chikamatsu M, Yoshida Y, Oishi M, Azumi R and Yase K 2008 *Appl. Phys. Express* **1** 0618021–3
[8] O'Connor B, Kline R J, Conrad B R, Richter L J, Gundlach D, Toney M F and DeLongchamp D M 2011 *Adv. Funct. Mater.* **21** 3697–705
[9] Morita T, Singh V, Nagamatsu S, Oku S, Takashima W and Kaneto K 2009 *Appl. Phys. Express* **2** 1–4
[10] Morita T, Singh V, Oku S, Nagamatsu S, Takashima W, Hayase S and Kaneto K *2010 Jpn. J. Appl. Phys.* **49** 0416011–5
[11] Noh J, Jeong S and Lee J-Y 2016. *Nat. Commun*. **7** 12374
[12] Pandey M, Nagamatsu S, Pandey S S, Hayase S and Takashima W 2016 *Org. Electron*. **38** 115–20
[13] Dauendorffer A, Miyajima S, Nagamatsu S, Takashima W, Hayase S and Kaneto K 2012 *Appl. Phys. Express* **5**
[14] Pandey M, Pandey S S, Nagamatsu S, Hayase S and Takashima W 2017 *J. Nanosci. Nanotechnol*. **17** 1915–22
[15] Pandey M, Nagamatsu S, Pandey S S, Hayase S and Takashima W 2016 *J. Phys. Conf. Ser*. **704** 12005
[16] Pandey M, Pandey S S, Nagamatsu S, Hayase S and Takashima W 2016 *Thin Solid Films* 619 125–30