Synthesis of Poly(3-butylthiophene) with Trisiloxane End Group and Its Surface Segregation Behavior in Thin Films

Fanji Wang1,2, Kazuhito Hashimoto2, Hiroshi Segawa3,4, and Keisuke Tajima1*

1 RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
2 Department of Applied Chemistry Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
3 Research Center for Advanced Science and Technology, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8904, Japan
4 Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan
*keisuke.tajima@riken.jp

A poly(3-butylthiophene) derivative with an end group of 1,1,1,3,3,5,5-heptamethyl trisiloxane group (P3BT-Si) was synthesized for the application of surface segregated monolayer (SSM) in polymer films. The surface segregation behaviors, thermal properties and chain orientation of P3BT-Si were investigated. The formation of the surface layer of P3BT-Si was confirmed in the blend films with polystyrene. In contrast to the fluoroalkyl-terminated polymer (P3BT-F17) that shows strong end-on orientation in the SSM with high crystallinity, P3BT-Si showed edge-on orientation in the SSM with low crystallinity. The difference can be attributed to the more flexible structure of trisiloxane group than the fluoroalkyl chain.

Keywords: Thin films, Semiconducting polymers, End-group functionalization, Low surface energy, Surface segregated monolayer, Trisiloxane

1. Introduction

During solution casting processes of organic semiconducting materials into the films, the molecules with the lower surface energy than the other components in the solution can spontaneously segregate onto the film surface to form a monolayer driven by the total energy minimization. This surface segregated monolayer (SSM) is a useful approach to modify the surface properties of the organic semiconducting films [1,2], and to alter the organic interfaces of donor/acceptor (D/A) in planar heterojunction (PHJ) organic photovoltaics (OPVs) [3-5] and the organic/metal interfaces in bulk heterojunction (BHJ) OPVs [6-8]. In addition, polymer-based SSM molecules showed strong preference of the molecular orientations in the surface layers depending on the substituent positions of the functionality with the low surface energy [9-11]. For example, poly(3-butylthiophene) with an end group of fluoroalkyl chain (P3BT-F17 in Fig. 1a) forms SSM on the polystyrene (PS) film in which the orientation of polymer main chains is vertical to the film surface (i.e. end-on orientation, Fig. 1c).

To give the low surface energy to the SSM molecules, fluoroalkyl chains have been mostly used to functionalize the organic semiconductors as in the case of P3BT-F17. The surface energy of the vertically aligned fluoroalkyl chains can be below 10 mN m⁻¹ [12]. However, the asymmetric fluoroalkyl chains have large permanent molecular dipole moments and the alignment of the molecules in SSM can induce a large shift of the vacuum levels at the film surface [3-5]. To observe the pure effects of the molecular orientations, it is sometime preferable to form SSM without the effects of the...
Oligosiloxane chains are also known to have a low surface energy (the surface energy of polydimethylsiloxane is 17 mN m\(^{-1}\)), which could be a potential candidate as the functionality to design the SSM molecules [7,13].

In this study, a new poly(3-butylthiophene) derivative with trisiloxane attached to a chain end (P3BT-Si in Fig. 1a) was synthesized for the application to SSM. The surface segregation and crystallization behaviors of P3BT-Si in thin films were investigated in comparison with those of P3BT-F\(_{17}\).

2. Experimental

Allyl-terminated P3BT (P3BT-allyl) was synthesized according to our previous report [14]. The number-average molecular weight (\(M_n\)) was 3900 with a polydispersity index (PDI) of 1.10. MALDI-TOF-MS measurement showed the peak with the maximum intensity at 1975.4 (-H/-allyl), which represents the polymerization degree of 14. Polystyrene (PS) with \(M_n\) of 6000 and PDI of 1.02 was purchased from Tosoh.

2.1. Synthesis of 1,1,1,3,3,5,5-heptamethyl trisiloxane-terminated poly(3-butylthiophene) (P3BT-Si)

A toluene (10 mL) solution of P3BT-allyl (200 mg, 0.10 mmol) and 1,1,1,3,3,5,5-heptamethyl trisiloxane (223 mg, 1 mmol) were placed in a 50 mL oven dried 2-necked round bottom flask flushed by N\(_2\) for 30 min. Karstedt catalyst (0.2 mL, 0.45 mmol) was subsequently added under N\(_2\), then the reaction mixture was stirred for 12 h at room temperature. After concentrated by vacuo evaporation, the dark purple solid was then dissolved in the minimum amount of CHC\(_3\) and precipitated into MeOH. The polymer was subsequently filtered and washed by MeOH, hexane, and CHC\(_3\) by Soxhlet extraction. After concentrated by vacuo evaporation, the dark purple solid was then dissolved in the minimum amount of CHC\(_3\) and precipitated into MeOH. The sediment was collected by filtration and dried under vacuum (150 mg, 71%).

2.2. Film preparation

Silicon substrates were washed by ultrasonication subsequently in detergent, pure water, acetone, 2-propanol, and pure water again for 30 min. Just before the use, the substrates were exposed to UV-O\(_3\) for 20 min. The P3BT-Si/PS sample was prepared by spin-coating of the blend solution of P3BT-Si (0.3-2.0 mg mL\(^{-1}\))/PS (3.5 mg mL\(^{-1}\)) in CHC\(_3\) on the silicon substrate at a speed of 1500 rpm for 60 s.

2.3. Characterizations

\(^1\)H NMR spectra were performed on a JEOL JNM-AL FT-NMR spectrometer utilizing CDCl\(_3\) as deuterated solvent. Gel permeation chromatography (GPC) was performed on a Shimadzu Prominence system equipped with a UV detector and SEC columns with CHC\(_3\) as the eluent at 40 °C. The wavelength of 500 nm was used to detect the polythiophenes. Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) was carried out in the reflection ion mode on a Bruker Daltonics Ultraflex-Ro spectrometer. Trans-2-[3-(4-t-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was utilized as the matrix for because it is a softer matrix requiring less laser intensity [15]. Differential Scanning Calorimetry (DSC) was performed on the Rigaku DSC at the heating speed of 10 K min\(^{-1}\) under N\(_2\). Optical microscopy was performed on a Nikon LV100TP-12. The XPS analysis was performed using a surface analysis apparatus (PHI 5000 VersaProbe II, ULVAC-PHI). Monochromated Al K\(_\alpha\) (1486.6 eV) radiation was used for all the XPS measurements. X-ray diffraction (XRD) analysis was performed on an X-
ray diffractometer (SmartLab, Rigaku, Japan) with monochromated CuKα radiation (λ = 0.154 nm) generated at 45 kV and 200 mA with an incident angle of 0.2°.

3. Results and discussion

The synthesis of P3BT-Si from P3BT-allyl was shown in Fig. 2a. The conversion to P3BT-Si was confirmed by 1H NMR in Fig. 2b. The disappearance of the peaks of allyl end group in P3BT-allyl at 3.49, 5.12, 5.97 ppm and the appearance of the peaks of the methyl groups on trisiloxane chains at 0.03 and 0.09 ppm indicate the complete conversion of P3BT-allyl to P3BT-Si. MALDI-TOF-MS measurement was also performed to verify the formation of P3BT-Si. As the result shown in Fig. 2c, the end group of P3BT-

Si can be assigned to either -Br/-trisiloxane or -H/-trisiloxane, also indicating the complete conversion to P3BT-Si. Note that complete conversion of the chain ends from -Br to -H would be possible by the reduction reaction with NaBH₄ [14]. However, we did not observe significant influence of -Br/-H ratio on the surface segregation behavior and the molecular orientation in the case of P3BT-F₁₇ [9,10]. Therefore, we speculate the effect of the end group is also small for P3BT-Si. The peak with the maximum intensity was 2199.6 that is corresponding to the polymerization degree (n) of 14. This value is the same as for P3BT-allyl precursor. GPC measurements showed that the Mₙ of P3BT-Si are 4100 with a PDI of 1.12, corresponding to n of 28. This overestimation of the molecular weight of poly(3-alkylthiophene)s by GPC by the factor of about 2 was previously reported [16].

The surface segregation behavior of P3BT-Si in P3BT-Si/PS films was investigated by XPS. The films were prepared by spin coating from CHCl₃ solutions of PS with a fixed concentration of 3.5 mg mL⁻¹ and the various concentrations of P3BT-Si (0.3-2.0 mg mL⁻¹). Figure 3 shows the Si/C atomic ratios determined by the intensities of Si 2p and C 1s peaks in XPS as a function of the concentrations of P3BT-Si in the blend solution. The linear increase of the Si/C atomic ratios determined by the intensities of Si 2p and C 1s peaks in XPS as a function of the concentrations of P3BT-Si in the blend solution. At the concentrations above 1.2 mg mL⁻¹, the Si/C atomic ratio was saturated at 0.032, suggesting the maximum coverage of the film surface with the trisiloxane moiety was reached. Note that a similar Si/C atomic ratio was observed on the surface of the pristine P3BT-Si film (0.033).
This value is only a little higher than the value calculated from the molecular formula (0.026 based on the assumption of the average $n$ of 14). This is in contrast to P3BT-F17 in which F/C atomic ratio at the film surface is much higher than those calculated from the molecular formula (0.27 vs. 0.11), suggesting the surface is preferentially covered with the fluoroalkyl chains [10]. Therefore, this result suggests that P3BT-Si segregate on the surface of PS film but P3BT-Si at the surface does not have strong preferential surface display of the trisiloxane moiety.

Based on the assumption that a uniform monolayer of P3BT-Si forms on the film surface with polymer chains aligned vertical at above the saturated concentration, Si/C ratio could be calculated by a bilayer model. The XPS intensity of the atoms in the trisiloxane end group (film) and polymer chains (substrate) can be expressed as [17,18]

$$\frac{I_{Si}}{I_C} = \frac{I_{Si}^0 X_{Si}}{I_C^0 X_C} \left[ \exp \left( \frac{d}{\lambda_C \cos \theta} \right) - \exp \left( \frac{d \lambda_{Si} - d \lambda_C}{\lambda_{Si} \lambda_C \cos \theta} \right) \right]$$

Fig. 4. Optical microscopic images of P3BT-Si/PS films (a) before thermal annealing and after annealing at (b) 120 °C, (c) 130 °C and (d) 150 °C for 2 h. (e) DSC trace of P3BT-Si powder in heating and cooling process at the rate of 10 K min$^{-1}$.

Fig. 5. (a) In-plane and (b) out-of-plane XRD patterns of P3BT-Si/PS (blue) and P3BT-F17/PS (red) film.

where $d$ is the thickness of trisiloxane layer, which was 0.67 nm estimated from optimized structure of the molecular model. $I_{Si}$ and $I_C$ are the XPS peak intensities. $X_i$ is the local concentration of the element $i$, for example, as we have 3 Si atoms in a 0.67 nm trisiloxane chain, $X_{Si}$ is 4.48. $\lambda_i$ is the attenuation length of the photoelectron, which Si 2p and C 1s are 2.9 and 3.8 nm, respectively, according to previous reports [19,20]. $\theta$ is the take-off angle and $I_i^0$ is the atomic relative sensitivity factor (RSF) of element $i$, which is supplied by the manufacturer of the XPS spectrometer. By setting the take of angle to be 0°, the calculated Si/C atomic ratio by this model was 0.054. The Si/C observed ratio at the saturated condition was about half of this calculated value. This result suggests that the density of the trisiloxane groups may not be as high as the ideal case of the bilayer model. In our previous work on P3BT-F17/PS, the F/C ratios observed at above the saturated concentration and the calculated ratio by using the bilayer model were close to each other; 0.272 and 0.283, respectively. This means that the SSM of P3BT-F17 has a high surface coverage on PS, leading to the highly ordered vertical alignment of the P3BT chains [11].

P3BT-Si (1.2 mg mL$^{-1}$)/PS (3.5 mg mL$^{-1}$) film at the saturated condition was selected to perform...
thermal annealing at different temperatures. The film morphology was observed by optical microscopy and the results were shown in Fig. 4. The films before and after annealing at 120 °C showed smooth and featureless surfaces (Figs. 4a and b). However, when the temperature was set to 130 °C, partial dewetting of the films was observed (Fig. 4c). The dewetting became severer in the whole film when the temperature was raised to 150 °C (Fig. 4d). Thermal property of P3BT-Si powder was studied by DSC (Fig. 4e). P3BT-Si showed clear melting and crystallization with crystallization (\(T_c\)) and melting temperatures (\(T_m\)) of 120 °C and 161 °C, respectively. On the other hand, glass transition temperature (\(T_g\)) of PS was reported to be 100-107 °C [21]. Considering the thermal behavior and the lowering of the surface energy, the monolayer of P3BT-Si at the surface of PS may help to maintain the film flatness and prevent PS in the bulk from dewetting. Above 120 °C, P3BT-Si at the surface start melting and the film start dewetting. On the other hand, in our previous report, P3BT-F\(_{17}\) showed higher \(T_c\) and \(T_m\) of 167 °C and 200 °C, respectively [14]. The flatness of P3BT-F\(_{17}\)/PS film could be maintained when annealed at 165 °C. The difference of \(T_c\) and \(T_m\) between P3BT-Si and P3BT-F\(_{17}\) can be attributed to the difference of their end groups. It has been reported that fluoroalkyl chains have rigid structure and could crystallize with a compact helical conformation [22]. In contrast, trisiloxane groups are known flexible and totally amorphous [23]. These flexible trisiloxane groups could have negative influence on the intermolecular packing of the polymer chains.

Finally, XRD analysis was performed on P3BT-Si (1.2 mg mL\(^{-1}\))/PS (3.5 mg mL\(^{-1}\)) film after thermal annealing at 120 °C to evaluate the chain orientation at the surface. P3BT-F\(_{17}\)/PS film was also prepared following the reported condition for comparison [10]. As shown in Fig. 5, P3BT-F\(_{17}\)/PS film showed clear peaks of both the lamellar at 6.5° (13.6 Å) and \(\pi-\pi\) stacking at 23.3° (3.8 Å) in in-plane direction, reproduced the results in the previous reports [9,10]. Two-dimensional grazing-incidence wide-angle X-ray scattering measurement on P3BT-F\(_{17}\)/PS sample in the previous report suggests that these diffraction signals have extremely narrow angle distributions only in the in-plane direction [9]. This indicates the formation of end-on oriented P3BT chains in the P3BT-F\(_{17}\) SSM with high order. In contrast, there is no peak observed in the in-plane direction and only a small peak appeared in the out-of-plane direction at 6.7° (13.2 Å) in P3BT-Si/PS film, which corresponds to the lamellar structure of P3BT. This result indicates that P3BT chains in the P3BT-Si SSM formed edge-on orientation on the surface of PS film with a low order. We attribute the difference in the chain orientation of P3BT between P3BT-F\(_{17}\) and P3BT-Si to the difference in the characteristics of the end groups and the crystallinity of the polymers. Unlike the rigid fluoroalkyl chain pointed up to the film surface forcing the polymer chain beneath aligned vertical, trisiloxane chain has a highly flexible structure [23]. This could provide the polymer chains with some space, allowing the interchain interactions in edge-on manner (Fig. 1b).

4. Conclusion

We investigated the trisiloxane group in P3BT-Si as the driver for SSM formation in the blend film with PS. P3BT-Si could form a low density SSM on top of the PS film, which prevent the film from dewetting after thermal annealing. However, P3BT chains in the SSM showed a low crystallinity with the molecular orientation of edge-on. This striking difference of the SSM behavior between P3BT-Si and P3BT-F\(_{17}\) suggests that not only the surface energy but also the flexibility of the end groups could be an important factor to achieve the well-ordered structures during the SSM formation.

Acknowledgements

This research was supported in part by Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST). F.W. thanks the Junior Research Associate (JRA) program of RIKEN for financial support.

References

1. Q. Wei, K. Tajima, Y. Tong, S. Ye, and K. Hashimoto, J. Am. Chem. Soc., 131 (2009) 17597.
2. Y. Geng, Q. Wei, K. Hashimoto, and K. Tajima, Chem. Mater., 23 (2011) 4257.
3. A. Tada, Y. Geng, Q. Wei, K. Hashimoto, and K. Tajima, Nat. Mater., 10 (2011) 450.
4. Y. Zhong, J. Ma, K. Hashimoto, and K. Tajima, Adv. Mater., 25 (2013) 1071.
5. S. Izawa, K. Nakano, K. Suzuki, K. Hashimoto, and K. Tajima, Adv. Mater., 27 (2015) 3025.
6. Q. Wei, T. Nishizawa, K. Tajima, and K. Hashimoto, Adv. Mater., 20 (2008) 2211.
7. S. Yamakawa, K. Tajima, and K. Hashimoto, Org. Elec., 10 (2009) 511.
8. F. Wang, K. Hashimoto, H. Segawa, and K. Tajima, ACS Appl. Mater. Interfaces, 10 (2018)
8901.
9. J. Ma, K. Hashimoto, T. Koganezawa, and K. Tajima, J. Am. Chem. Soc., 135 (2013) 9644.
10. F. Wang, K. Hashimoto, and K. Tajima, Adv. Mater., 27 (2015) 6014.
11. J. Ma, K. Hashimoto, T. Koganezawa, and K. Tajima, Chem. Commun., 50 (2014) 3627.
12. D. K. Owens and R. C. Wendt, J. Appl. Polym. Sci., 13 (1969) 1741.
13. S. Izawa, K. Nakano, K. Suzuki, Y. Chen, T. Kikitsu, and D. Hashizume, Sci. Rep., 8 (2018) 481.
14. J. Ma, Y. Geng, K. Hashimoto, and K. Tajima, Macromol. Chem. Phys., 214 (2013) 1326.
15. J. D. Winter, G. Deshayes, F. Boon, O. Coulembier, P. Dubois, and P. Gerbaux, J. Mass Spectrom., 46 (2011) 237.
16. J. Liu, R. S. Loewe, and R. D. McCullough, Macromolecules, 32 (1999) 5777.
17. C. Ton-That, A. G. Shard, and R. H. Bradley, Langmuir, 16 (2000) 2281.
18. M.-W. Tsao, J. F. Rabolt, H. Schönherr, and D. G. Castner, Langmuir, 16 (2000) 1734.
19. H. Yokoyama, K. Tanaka, A. Takahara, T. Kajiyama, K. Sugiyama, and A. Hirao, Macromolecules, 37 (2004) 939.
20. H. Ebel, C. Pöhn, R. Svagera, M. E. Wernle, M. F. Ebel, and A. Jablonski, J. Electron. Spectrosc. Relat. Ph., 50 (1990) 109.
21. J. Rieger, J. Thermal Anal., 46 (1996) 965.
22. K. Honda, M. Morita, H. Otsuka, and A. Takahara, Macromolecules, 38 (2005) 5699.
23. J. E. Mark, Acc. Chem. Res., 37 (2004) 946.