Novel highly ordered Langmuir–Blodgett films of regioregular poly(3-substituted thiophene)

Keiko Ochiai,[ab] Masahiro Rikukawa*[ab] and Kohei Sanui[ab]

[a] *Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan.*
E-mail: m-rikuka@hoffman.cc.sophia.ac.jp
[b] *CREST, Japan Science and Technology Corporation (JST), 4-1-8 Hon-cho, Kawaguchi, Saitama, 332-0012, Japan*

Received (in Cambridge, UK) 1st March 1999, Accepted 7th March 1999

Langmuir–Blodgett films have been fabricated from a regioregular poly(thiophene) derivative by the vertical dipping method while still maintaining the high self-organization associated with the regioregularity of the polymer.

A great deal of progress has been made towards the molecular engineering of conducting polymers that allow us to control nanoscopic structure and that possess exceptional properties. Many of the important advances in this area have centered on the synthesis of structurally homogeneous materials.[1,2] Most notably, the recent development of regioregular conducting polymers based on 3-substituted poly(thiophenes) has heralded a new direction for molecular engineering research.[3–6] These regiochemical arrangements provide an opportunity to understand structure–property relationships in conducting polymers with enhanced electrical and optical properties. It has been recognized that electrical and optical properties based on conjugated systems strongly depend on their nano-structural organization, which can be controlled by the introduction of functional groups and regioregularity. To date, however, only conventional solution casting and spin-coating methods, which offer very little control over molecular order and organization of the polymer, have been utilized to process the novel regioregular polymers. We have recently shown that it is possible to fabricate Langmuir–Blodgett (LB) thin films from mixed monolayers containing stearic acid and regioregular poly(3-alkylthiophenes).[7–9] This novel approach results in well-defined and controllable molecular architectures with desirable optical and electrical properties. We now report further work aimed at fabricating highly ordered LB films of regioregular poly(3-{2-[(*S*)-2-methylbutoxy]ethyl}thiophene) [P(S)MBET] without stearic acid as an amphiphilic molecule. The influence of regioregularity on LB manipulation and solid state structure is also discussed by comparing the monolayers of regioregular and regiorandom P(S)MBET.

The regioregular poly(thiophene) derivative, head-to-tail poly(3-{2-[(*S*)-2-methylbutoxy]ethyl}thiophene) [*HT*-P(S)MBET], was synthesized according to the modified Rieke method.[3] *HT*-P(S)MBET was an optically active polymer with > 93%e head-to-tail linkages, as determined from NMR data.[10] Regiorandom P(S)MBET [*R*-P(S)MBET] with 54% head-to-tail linkages was also prepared by the same catalytic polymerization with $Pd(PPh_3)_4$. *HT*-P(S)MBET used in this study had $M_w = 2.15 \times 10^4$, $M_n = 1.56 \times 10^4$ and $M_w/M_n = 1.38$, while *R*-P(S)MBET had $M_w = 2.05 \times 10^4$, $M_n = 1.02 \times 10^4$, and $M_w/M_n = 2.02$. Since the transfer ratios and the collapse pressures of the monolayer increased with decreasing temperature, LB monolayer and multilayer thin films were fabricated using a Lauda film balance at 10 °C. Monolayers were spread from $CHCl_3$ solutions on a purified aqueous subphase.[11,12]

In order to manipulate soluble conducting polymers into LB films, it is normally necessary to utilize amphiphilic molecules that are capable of forming monolayers at the air–water interface of an LB trough. Thus, poly(3-alkylthiophenes) cannot be formed directly into monolayers owing to the lack of a strong dipole. For example, the spreading of a $CHCl_3$ solution containing poly(3-hexylthiophene) onto the air–water interface of an LB trough simply results in the formation of aggregated islands of the polymer which only exhibit a surface pressure when they are forced together into a very small molecular area. Regioregular poly(3-hexylthiophene) also shows similar phenomena even if the higher regioregularity provides a more coplanar structure of thiophene rings and leads to higher rigidity in the monolayers. Highly ordered LB films of regioregular and regiorandom poly(3-alkylthiophenes) can be easily fabricated by mixing the polymer with suitable portions of an amphiphilic molecule such as stearic acid.[7–9]

HT-P(S)MBET and *R*-P(S)MBET were spread from a $CHCl_3$ solution on the water surface to measure the π–A isotherms at 10 °C. (Fig. 1). *HT*-P(S)MBET monolayers exhibit a stable condensed solid phase with a phase transition at about 18 mN m^{-1}. It is of interest that both the π-A isotherms show a relatively steep rise at a large molecular area. The area per molecule of *HT*-P(S)MBET was estimated to be 17 Å^2 per polymer repeat unit, which was larger than that for head-to-tail poly(3-hexylthiophene) (*HT*-PHT) (about 8 Å^2).[7–9] According to the CPK model, 17 Å^2 corresponds with the cross section of the thiophene ring of *HT*-P(S)MBET. As the most probable molecular orientation, the coplanar poly(thiophene) backbones float on the water surface and the side chains on one side of the zigzag formation orient toward the water phase. In contrast, the monolayer of *R*-(S)MBET shows a larger molecular area (19 Å^2) and lower collapsed pressure (10 mN m^{-1}), indicating that *R*-P(S)MBET molecules randomly orient and the monolayer is relatively unstable compared with *HT*-P(S)MBET. These results clearly demonstrate that the methylbutoxyethyl groups of P(S)MBET provide suitable dipoles for forming monolayers

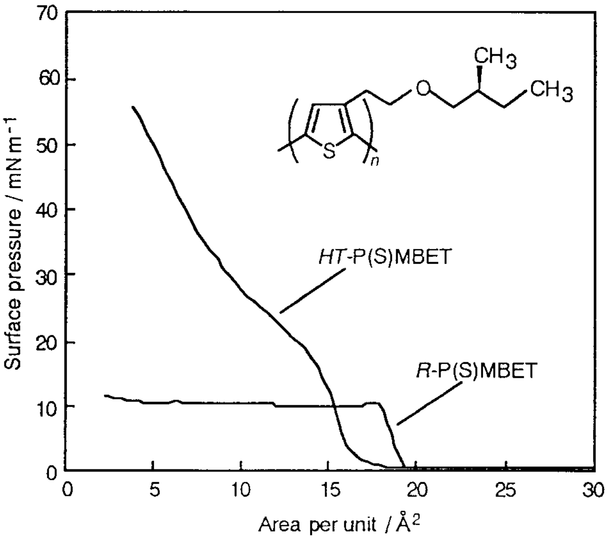

Fig. 1 Surface pressure–area isotherms of *HT*-P(S)MBET and *R*-P(S)MBET monolayers at 10 °C.

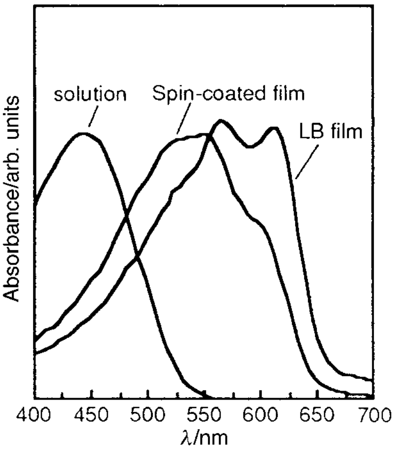

Fig. 2 UV–VIS spectra of *HT*-P(S)MBET in $CHCl_3$, an *HT*-P(S)MBET spin-coated film, and an *HT*-P(S)MBET LB film.

on the air–water interface. We further found that the higher regioregularity gives self-organized structures and induces rigid and coplanar main-chain structures that are capable of forming stable condensed solid monolayers at the air–water interface.

The *HT*-P(S)MBET LB films can be produced by the standard Langmuir–Blodgett vertical dipping method. Optical absorption measurements made on stepped films as a function of the number of layers deposited indicate that the *HT*-P(S)MBET is transferred reproducibly into the multilayer films, while multilayer thin films could not fabricated from *R*-P(S)MBET monolayers on the air–water interface due to the instability of the condensed monolayers. As shown in Fig. 2, the maximal absorption of the *HT*-P(S)MBET LB film shows lower π–π* transition energy than that of the spin-coated film, while the intensity of the shoulder for the LB film at the longer wavelength around 610 nm is relatively stronger than that of the spin-coated film. These spectra also indicate that *HT*-P(S)MBET molecules in the LB films have a more planar conformation with longer conjugation length compared with the spin-coated films of *HT*-P(S)MBET. Further, it is found from the polarized UV-VIS absorption spectra that *HT*-P(S)MBET molecules in the LB films are oriented parallel to the plane of the substrate and have a tendency to orient along the dipping direction. In practice E_p/E_s was about 1.5, where E_p and E_s were the absorbances of light polarized with the electric vector parallel and perpendicular respectively to the direction of dipping of the substrate. Thus, the LB technique provides molecular control over the regioregular polymers to form better-organized structures that exhibit more planar conformations with low band-gaps and with anisotropic orientations of polymer chains.

The X-ray diffraction pattern of an *HT*-P(S)MBET LB film is shown in Fig. 3. The presence of at least three Bragg diffraction peaks clearly demonstrates that we have formed a well-defined layered structure with a repeat distance of around 18 Å, which is identical to the interlayer *d*-spacing of well-organized lamellar structure for *HT*-P(S)MBET spin-coated films. These results suggest that *HT*-P(S)MBET molecules in the LB films maintain the high self-organization associated with the regio-regularity and adopting a crystalline, self-organized lamellar morphology with three dimensional ordering of the polymer chains such as is observed for regioregular poly(3-alkyl-thiophene) cast films. Ultrathin films with lamellar morphology artificially built up were produced for the first time.

3-Substituted poly(thiophenes) with regioregular structures are expected to be highly ordered and therefore to exhibit improved electrical and optical properties. These highly-ordered LB films are readily doped with oxidizing agents such as nitrosyl hexafluorophosphate and ferric chloride to produce electrically conductive multilayer thin films. To date, we have been able to reach in-plane conductivity of about 1-5 S cm^{-1}, which is 10^4- to 10^5-fold higher than *R*-P(S)MBET spin-coated films. Our films also exhibit highly anisotropic behavior in electrical conductivity to the dipping direction. In addition, preliminary results have shown that these LB films exhibit enhanced optical nonlinear susceptibility $\chi^{(3)}$.

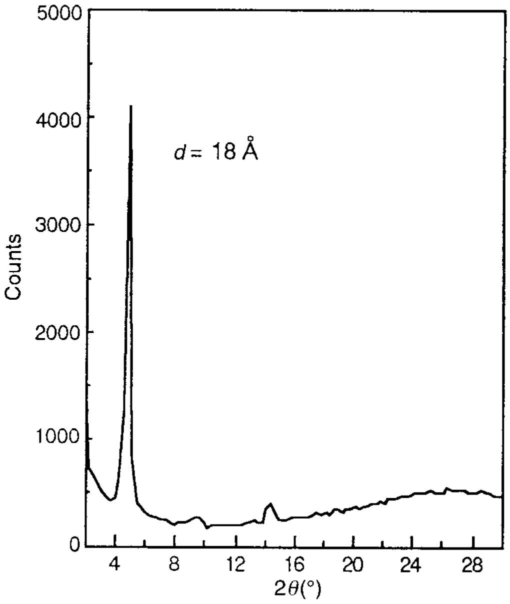

Fig. 3 X-Ray diffraction pattern of an LB film (10 layers) of *HT*-P(S)MBET.

In summary, we have presented a method for the synthesis and thin film formation of regioregular P(S)MBET, which results in a large improvement in electrical and optical properties. We believe that the introduction of regioregularity and suitable functional groups results in better molecular organization and this in turn results in the excellent optical and electrical properties of these interesting materials.

Notes and references

1 N. Basescu, Z.-X. Liu, D. Moses, A. Heeger, H. Naarmann and N. Theophilou, *Nature*, 1987, **327**, 403.

2 D. L. Gin, V. P. Conticello and R. H. Grubbs, *J. Am. Chem. Soc.*, 1992, **114**, 3167.

3 T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233.

4 T.-A. Chen and R. D. Rieke, *Synth. Met.*, 1993, **60**, 175.

5 R. D. McCullough, R. D. Lowe, M. Jayaraman and D. L. Anderson, *J. Org. Chem.*, 1993, **58**, 904.

6 R. D. McCullough and R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, 70.

7 M. Rikukawa, M. Nakagawa, H. Abe, K. Sanui and N. Ogata, *Thin Solid Films*, 1996, **284–285**, 636.

8 M. Rikukawa, M. Nakagawa, H. Abe, K. Ishida, K. Sanui and N. Ogata, *Thin Solid Films*,1996, **273**, 240.

9 M. Rikukawa, M. Nakagawa, Y. Tabuchi, K. Sanui and N. Ogata, *Synth. Met.*, 1997, **84**, 233.

10 M. Sato and H. Morii, *Macromolecules*,1991, **24**, 1196.

11 K. Ochiai, Y. Tabuchi, M. Rikukawa, K. Sanui and N. Ogata, *Thin Solid Films*, 1998, **327–329**, 454.

12 S. Kishino, Y. Ueno, K. Ochiai, M. Rikukawa, K. Sanui, T. Kobayashi, H. Kunugita and K. Ema, *Phys. Rev. B*, 1998, **58**, 430.

Communication 9/01617A