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RAPID COMMUNICATION

Microscopic conduction pathways of poly (3-hexylthiophene) nanofibers embedded in polymer film

INTRODUCTION

Conjugated conducting polymer nanofibers have recently attracted increasing interest for applications, such as molecular electronics, conductive inks for printable electronics and organic field-effect transistors (OFETs).[1–3] Polythiophene derivatives including poly(3-alkylthiophenes) (P3ATs) are among the most promising conducting polymers, because in addition to high carrier transport based on the π-conjugated polythiophene chains, the alkyl side chains of P3ATs enable them to be dissolved in common organic solvents. Thus, solvent-soluble P3ATs are suitable for the formation of nanofibers using solution-based techniques, and in particular, by means of the whisker method using organic solvents.[4–7]

An attractive feature of the solution-based process is that different materials can be easily blended to optimize the electrical and mechanical properties according to the device application. OFETs, based on poly(3-hexylthiophene) (P3HT), as a conjugated conducting polymer embedded in the insulating matrix of a polymer film have been reported. These reports suggest that control of phase separation of the conjugated conducting polymer is quite important to form a continuous nanofiber network and exhibit the OFET effect.[8–10]

The electrical percolation behavior in the bulk polymer and on the surfaces of organic electronics containing conducting nanofibers is strongly influenced by the condition of the nanofiber network. Therefore, we have directed our attention to investigation of the microscopic conduction pathways in a nanofiber network of regioregular P3HT (rr-P3HT). Kelvin probe force microscopy (KFM) was employed to investigate the conduction pathways of the nanofiber network. KFM is a useful tool to simultaneously investigate the

microscopic topography with atomic force microscopy operation, and the local potential on the surface by the vibrating capacitor method, that is, the Kelvin method.[11–13] In this study, the whisker method was applied using a solvent mixture of anisole and chloroform[5–7] to form the P3HT-conducting nanofiber network of rr-P3HT embedded in a poly(methyl methacrylate) (PMMA) matrix as an insulating intermediate.

EXPERIMENTAL PROCEDURE

rr-P3HT (Mw=87 000) and PMMA (Mw=120 000) were purchased from Aldrich Co. Inc. (St Louis, MO, USA) and used without further purification. Conducting P3HT nanofibers were embedded in PMMA as follows.[8] A 1–2 wt% solution of a polymer blend consisting of rr-P3HT and PMMA with a ratio of 1:99 (w/w) was prepared using an organic solvent mixture of anisole and chloroform (50:50, v/v), with stirring at 50 °C. The solution was continuously stirred and gradually cooled from 50 °C to room temperature at a rate of 20 °C h^{-1}. A 1 wt% solution of the polymer blend with only chloroform was also prepared as a reference.[8]

Pt electrodes (0.6 mm long) with a gap space of 40 μm were fabricated with a bottom-contact configuration by sputter deposition, using a shadow mask on a piece of Si wafer with a 255-nm thermally grown SiO$_2$ layer on top (SiO$_2$/Si; KST World Corp., Fukui, Japan). Thin films of P3HT/PMMA were prepared by spin-coating at 3000 r.p.m. for 30 s on the SiO$_2$/Si substrate with Pt electrodes, and the residual solvent on the substrate was removed by vacuum drying. For the top-contact configuration, the same Pt electrodes were fabricated after P3HT/PMMA thin films were cast on a bare SiO$_2$/Si substrate using the same spin-coating conditions.

The thin films of P3HT/PMMA were observed in air with a CP-II scanning probe microscope (Veeco Instruments Inc., Plainview, NY, USA) equipped with a lock-in amplifier, an interface module, an ac voltage source and a dc voltage source for KFM observation. A Pt-coated Si cantilever (OMCL-AC-240TM, Olympus, Tokyo, Japan); spring constant 2 N m^{-1}, resonant frequency 70 kHz) was used in intermittent-contact mode. A dc-biased sinusoidal voltage of 5 V at a frequency of approximately 17 kHz was applied between the probe and the sample as the probe electrical signal for the surface potential measurement with the Kelvin method. The electrical conductance of the P3HT/PMMA thin films was measured using a Keithley 236 source measure unit (Keithley Instruments, Inc., Cleveland, OH, USA).

To confirm the influence of the electrode configurations, we performed FET measurements of P3HT nanofibers without a PMMA matrix formed by the whisker method as reported elsewhere.[5–7] FETs were composed with SiO$_2$/Si substrate, on which P3HT nanofibers were spin-coated and Pt electrodes were sputtered as the source and drain electrodes. The Pt electrodes with the top- and bottom-contact configurations were fabricated using the same methods for the thin films of P3HT/PMMA described above.

The FET measurements were executed in vacuum ($<10^{-5}$ Torr) at room temperature, using a combined system of the probe station chamber (ARK-LIPS-LV-2, Nagase Electronic Equipment Service Co., Ltd, Tokyo, Japan), the Keithley 236 source measure unit to measure the source–drain characteristics I_{SD}, and a digital sourcemeter (Keithley 2400, Keithley Instruments, Inc.) to apply the gate voltage V_G from backside gate.

RESULTS AND DISCUSSION

The topographic image of the P3HT/PMMA thin film cast from chloroform solution shown in Figure 1a indicates that no nanofibers were formed. In the phase separation process of P3HT in polymer blends, there has been no report of nanofiber formation when only chloroform is used as a solvent,[9] which is consistent with the present work. Furthermore, the electrical conductance was less than 10^{-11} S and the thin film was almost insulative. On the contrary, the topographical image of the thin film formed using the anisole/chloroform solvent mixture (Figure 1b) confirms that conducting P3HT nanofibers were formed in the PMMA matrix. In addition, the thin film of P3HT/PMMA formed with the solvent mixture exhibited much higher conductivity (7.0×10^{-8} S), which was measured for the bottom-contact configuration. These results indicate that the P3HT nanofibers were well formed in the PMMA matrix using the whisker method with adequate solvent (anisole/chloroform mixture). The bulk conductivity of the film prepared under these conditions was significant, which indicates that the P3HT nanofibers are electrically connected over the entire bulk film, like a circuit network, and therefore, have a large influence on the film conductivity.

To confirm electrical percolation in the nanofibers of the film, the surface potential of the nanofiber network was measured using KFM, with the application of an external potential bias at 500 mV from the Pt electrodes with bottom-contact configuration using a function generator (DF1906, NF Corp., Yokohama, Japan). Figures 2a and b show topographic images of the film surface opposite to the electrodes when applying low (0 V) and high voltages (500 mV), respectively. Figures 2c and d show surface potential images that correspond to Figures 2a and b, respectively. Nanofibers corresponding to those observed in the topographical images were clearly observed in the surface potential images, and the brightness gradually decreased from high voltage side to the low side. The cross section in the low side (Figure 3) shows that the surface potential of the nanofibers was raised to approximately 470 mV, with respect to that of the matrix. These results suggest that the electrical potential applied from the bottom-contact electrodes was percolated to the film surface through the nanofibers, forming a three-dimensional network with the electrical connections, and that the bare nanofibers on the film surface are biased with the externally applied voltage. On the other hand, the higher surface poten-
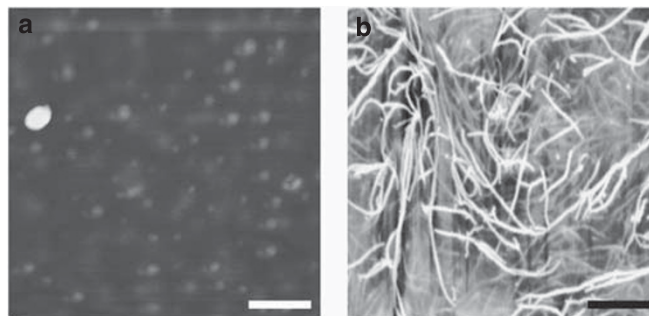

Figure 1 Scanning probe microscope topographical images of P3HT/PMMA thin films produced using (**a**) only chloroform, and (**b**) an anisole/chloroform (50:50, v/v) solvent mixture. Scale bars in (**a**) and (**b**) are 1 and 5 μm, respectively. A full color version of this figure is available at *Polymer Journal* online.

Figure 2 (**a**, **b**) Topographical and (**c**, **d**) surface potential KFM images of the bottom-contact configuration P3HT/PMMA thin film externally biased at 500 mV (high side in (**a**) and (**c**), and low side in (**b**) and (**d**)). Two captures were obtained with overlapping. Scale bars are 5 μm. A full color version of this figure is available at *Polymer Journal* online.

tial of the matrix in the high side than that of the low side indicates that nanofibers were not bared on the film surface, but embedded in the matrix as shown in the topographical images, influence the surface potential of the matrix. Therefore, the potential difference between the nanofibers and the matrix in the high side decreased to approximately 260 mV.

KFM observations were also performed with the top-contact configuration to confirm the conduction pathway from the electrodes to the nanofibers. The topographical images around the electrodes applying low (0 V) and high voltages (500 mV) are shown in Figures 4a and b, respectively, and Figures 4c and 4d show the corresponding surface

potential images. The electrodes were clearly evident in both the topographical and surface potential images. In contrast, nanofibers within the region 10 μm from the electrodes were not clearly evident in the surface potential images, although nanofibers were observed in the entire electrode gap region, as evident in the topographical images. This tendency was independent of the scan direction and scan rate. On the other hand, the film conductivity in the top-contact configuration was 2.9×10^{-8} S, which was comparable to that for the bottom-contact configuration with similar film thickness; therefore, the conduction pathways were connected from one electrode to the counter electrode. These results suggest that the

Figure 3 Cross section of the surface potential along the line indicated by a–b in Figure 2c.
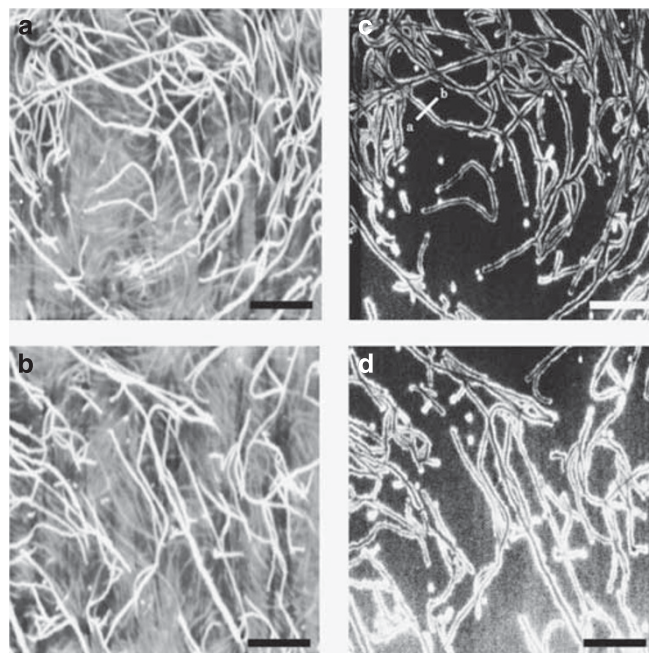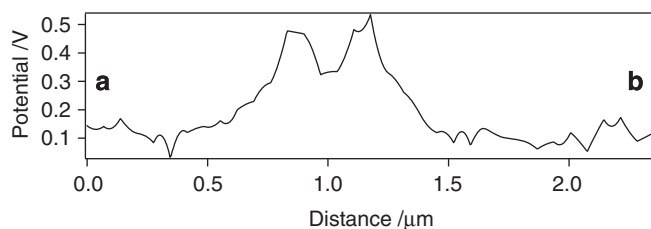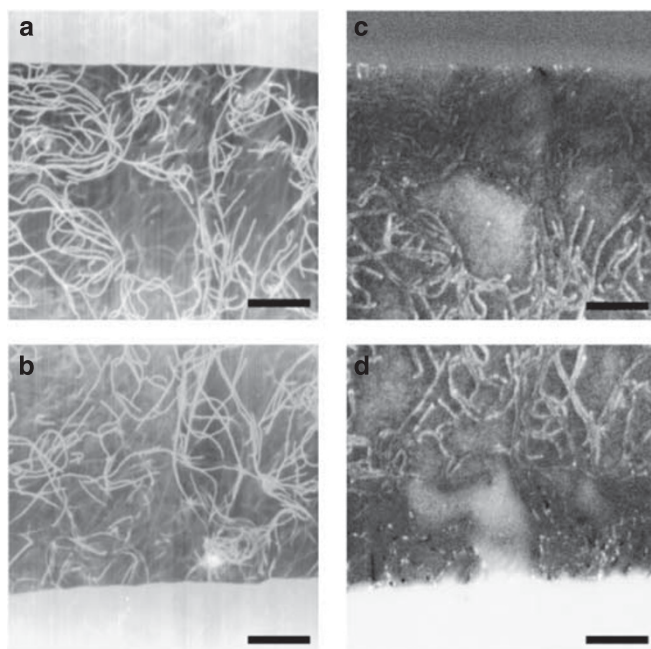

Figure 4 (a, b) Topographical and (c, d) surface potential KFM images of the top-contact configuration P3HT/PMMA thin film externally biased at 500 mV (high side in (a) and (c), and low side in (b) and (d)). Two captures were obtained with overlapping. Scale bars are 5 μm. A full color version of this figure is available at *Polymer Journal* online.
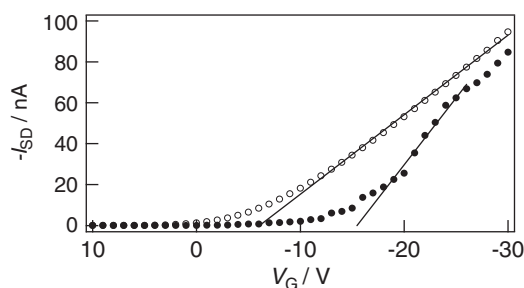

Figure 5 FET transfer characteristics of P3HT nanofibers without a PMMA matrix, where solid lines show the fitting characteristic with a linear relationship. Filled and open circles represent top- and bottom-contact configurations, respectively.

the film surface near the electrodes did not exhibit a surface potential, the conduction pathways were connected between the electrodes via the interior of the film. Furthermore, the nanofibers near the electrodes appeared to be damaged by the sputtering process on the film through processes, such as thermal stress, in the microscopic crystallinity of the nanofibers, and hence, the electrical structures, that is, conjugated chains.

Moreover, as shown in Figure 5, the FET transfer characteristics of P3HT nanofibers without a PMMA matrix were measured with the top- and bottom-contact configurations, applying a source–drain voltage V_{SD} of -5 V. The p-type semiconductor characteristic feature in both configurations was observed and the negative threshold gate voltage for the top-contact configuration was higher than that with the bottom-contact configuration. The field-effect mobility μ for each configuration was calculated from the gradient of linear regime using the following relationship:

$$\frac{dI_{SD}}{dV_G} = \frac{W}{L} \mu C_{OX} V_{SD}$$

where L ($=40$ μm) is the spacing of electrodes, W ($=0.6$ mm) is the effective width of electrodes, and C_{ox} ($=13.8$ nF cm^{-2}) is the capacitance per unit area of the SiO$_2$-insulating ayer with a thickness of 255 nm. The field-effect mobility with the bottom-contact configuration was estimated to be 3.7×10^{-3} cm^2 V^{-1} s^{-1}, which was the same order as that reported previously.[7] On the other hand, the estimated field-effect mobility with the top-contact configuration was 6.3×10^{-3} cm^2 V^{-1} s^{-1}, which was higher than that with the bottom-contact configuration; however, this does not indicate that the FET transfer characteristic in the top-contact configuration was higher than that in the bottom-contact configuration, as I_{SD} in the top-contact configuration approximated to that in the bottom-contact with increasing the negative gate voltage. These differences in the FET transfer characteristics between the top- and bottom-contact configurations indicate that a charge trap ascribed to damaged the nanofibers or substrate was generated by the sputtering process in the top-contact configuration, and is consistent with the KFM measurement of P3HT nanofibers embedded in a PMMA matrix.

In conclusion, the microscopic structures and electrical properties of P3HT nanofibers embedded in the PMMA matrix were investigated using KFM. This study demonstrated that the conducting nanofibers formed a three-dimensional network with electrical connections, which had a significant influence

conduction pathways of the film in the top-contact configuration are formed as follows. The electrical flux in the top-contact configuration is at first not parallel to the film surface, but directly perpendicular from the electrode to the interior of the film. And then, the electrical flux leaves for the counter electrode with spreading to the bulk, including the film surface apart from the electrodes, along the nanofibers. Therefore, the nanofibers on the film surface apart from the electrodes exhibited the surface potential that reflected the applied voltage in KFM observation and, although the nanofibers on

on the electrical properties of the polymer films as conduction pathways.

The microscopic structures and electrical properties of regioregular poly(3-hexylthiophene) (P3HT) nanofibers embedded in a poly(methyl-methacrylate) film as an insulating intermediate by means of whisker method has been investigated using the Kelvin probe force microscopy. This study demonstrated that the conducting P3HT nanofibers formed a three-dimensional network with electrical connections, which had a significant influence on the electrical properties of the polymer films as conduction pathways.

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