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Alignment and Field-Effect Transistor Behavior of an Alternative π-Conjugated Copolymer of Thiophene and 4-Alkylthiazole

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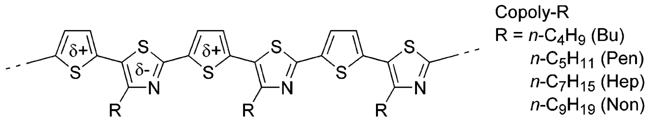
Charge-transfer-type π-conjugated copolymer of thiophene and 4-alkylthiazole is aligned on the surface of a platinum substrate, with the alkyl groups oriented toward the surface of the substrate. The copolymer served as a good material for a polymer field-effect transistor and gave a mobility of 2.5×10^{-3} cm^2 V^{-1} s^{-1}.

Introduction

The synthesis of π-conjugated polymers and the application of such polymers to electronic and optical devices have been subjects of recent interest.[1] There has been growing interest in the molecular alignment of π-conjugated polymers on substrates [2−4] because of the potential improvement of the electronic and optical properties of the π-conjugated polymer (e.g., for increasing the mobility of carriers in the polymer[2a,c]).

The π-conjugated polymer with a long side chain (e.g., head-to-tail-type poly(3-alkylthiophene), HT-P3RTh) often assumes an end-on[3a] type alignment with the alkyl side chains oriented toward the surface of the substrate, particularly when the polymer has a regioregular structure and forms a π-stacked structure.[2d−f,4a,e]

We previously reported the preparation of a regioregular HT-type charge-transfer (CT)-type copolymer of electron-donating thiophene and electron-accepting 4-alkylthiazole.[5]



The copolymer is considered to form the stacked structure depicted in Figure 1a, and the UV−vis absorption peak of Copoly-Non (R = nonyl) in solutions showed a large shift to a longer wavelength in the solid state.

For example, the UV−vis spectrum of Copoly-Non at approximately 460 nm in solutions (chloroform and trifluoroacetic acid) shifts to approximately 600 nm in a cast film and colloidal solutions.[5,6] The large shift of the UV−vis absorption peak suggests the presence of a strong face-to-face interplane stacking interaction between the Copoly-R molecules in the solid. Because such π-conjugated polymers with the strong interplane stacking interaction may have a tendency to form the above-described ordered structure on the surface of substrates, we investigated the packing structure of the film of Copoly-R formed on a Pt plate first.

By the way, various research studies have been carried out for the application of electron-donating

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(6) The Copoly-Non gave two peaks at approximately 580 and 620 nm in the cast film and colloidal solutions,[5] presumably due to separation of the peak by a vibronic coupling. When the film was prepared by casting from a trifluoroacetic acid solution of the copolymer, two kinds of treatments of the film were made. One film was prepared by drying under vacuum without pretreatment with aqueous ammonia and contained a small amount of trifluoroacetic acid, and another was dried under vacuum after pretreatment with aqueous ammonia and was free from trifluoroacetic acid (proved by IR). The two polymer films showed essentially the same UV−vis absorption pattern.

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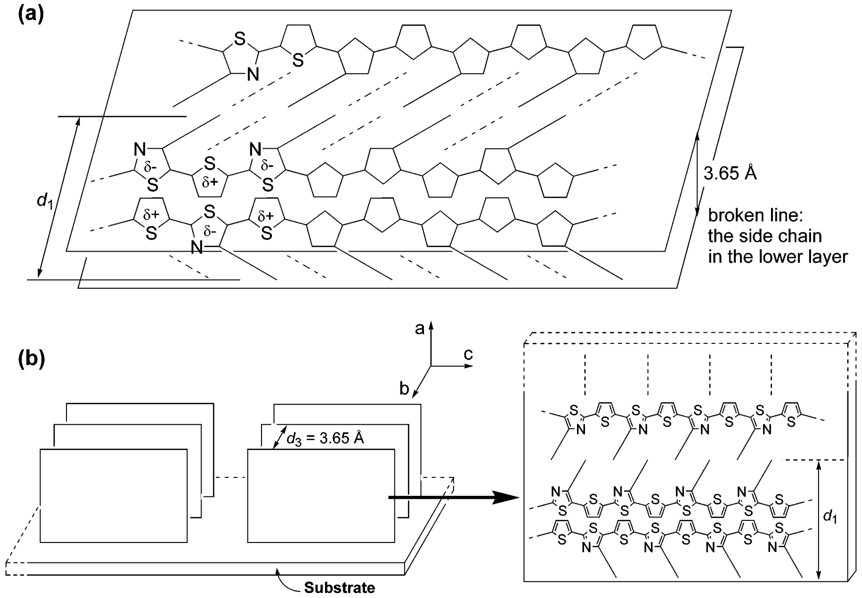

Figure 1. (a) Interplane stacking structure of Copoly-R. (b) Alignment of Copoly-R on the surface of the Pt plate. The R groups are oriented toward the surface of the Pt substrate.

p-type π-conjugated polymers to field-effect transistors (FETs).[1,2,7] However, the application of such CT-type π-conjugated polymers as shown above to FETs has not been explored much. On this basis, we investigated the applicability of Copoly-R in FETs. Herein, we report (i) that Copoly-R actually forms such an ordered structure as depicted in Figure 1b, similar to the case of HT-P3RTh,[2c−f,4a] and (ii) that Copoly-R can serve as a good active material for FETs.

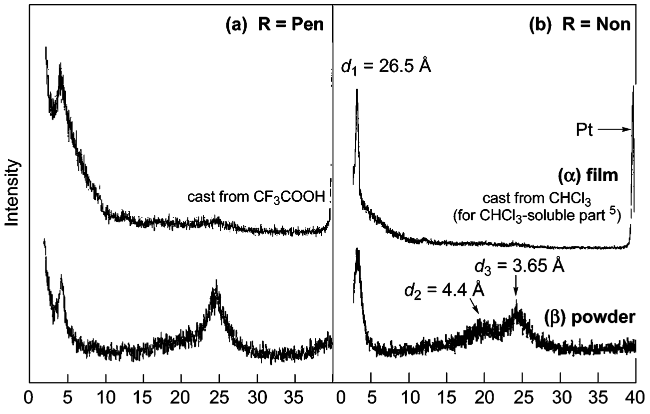

Figure 2. Comparison of XRD patterns of the cast film of Copoly-R (upper curve (α)) and powdery Copoly-R (lower curve (β)): (a) for R = Pen, and (b) for R = Non; casting from trifluoroacetic acid gives essentially the same XRD pattern. The XRD patterns were measured with a symmetrical-reflection technique.[4a]

Results and Discussion

Alignment. Figure 2 shows X-ray diffraction (XRD) patterns of Copoly-Pen (R = pentyl) and Copoly-Non (R = nonyl) with cast films on a Pt plate and powdery samples. The XRD patterns were measured with a symmetrical-reflection technique and gave information with regard to the direction of depth for the film samples.

As can be seen from Figure 2, both the film and powdery samples give the d_1 peak corresponding to the distance between the doubly running main chains of Copoly-R separated by the R groups (cf. Figure 1).[5] However, the d_2 and d_3 peaks observed with the powdery samples are not observed with the cast films. The d_2 and d_3 peaks are assigned to a side-to-side distance between the R side chains and to an interplane distance (3.65 Å) of stacked Copoly-R, respectively.[5]

Similar differences between the XRD patterns of powdery and cast film samples of π-conjugated polymers with long side chains and high regioregularity have been reported,[2,4a,e] and the difference is considered to originate from the alignment of the π-conjugated polymer on substrates, with the R side chain oriented toward the surface of the substrate. The cast film of Copoly-Pen on a hexamethyldisilazane (HMDS)-treated silicon wafer gave essentially the same XRD pattern, indicating that the polymer assumes an analogous ordered structure on the HMDS-treated silicon wafer substrate.

Although the XRD pattern measured with the symmetrical-reflection technique (cf. Figure 2) shows neither the d_2 nor d_3 peaks, an in-plane XRD pattern of the spin-coated film of Copoly-Pen of the Pt substrate clearly exhibits the d_2 peak. The d_1 peak is not clearly observed in the in-plane XRD pattern, because the in-plane XRD pattern does not give the peak due to the layers formed in the direction of depth of the film. The present results provide another example that the π-conjugated polymer with long side chains and a strong interlayer stacking interaction can form such an aligned structure with the side chain oriented toward the surface of the substrate.

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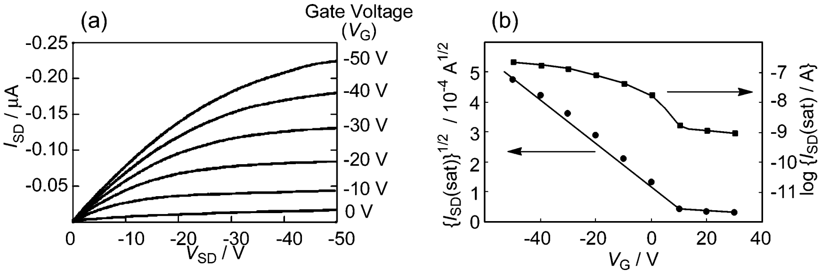

Figure 3. (a) $I_{SD}-V_{SD}$ curve for the FET prepared using Copoly-Non (I_{SD} = source-drain current, V_{SD} = source-drain voltage), and (b) plots of $\{I_{SD}(\text{sat})\}^{1/2}$ and log$\{I_{SD}(\text{sat})\}$ vs V_G. Channel length (L) = 50 μm. Channel width (W) = 250 μm. Thickness of the polymer film = approximately 30 nm.

Field-Effect Transistor (FET). Figure 3a exhibits I_{SD} (source-drain current)$-V_{SD}$ (source-drain voltage) curves observed with a FET fabricated using Copoly-Non at various gate voltages (V_Gs). To avoid the effect of acids such as CF_3COOH, a chloroform-soluble part of Copoly-Non was used and the polymer film was cast from chloroform. As shown in Figure 3a, the curve shows the saturation characteristics of FETs including previously reported polymer FETs.[7,8] I_{SD} is controlled by V_G applied through the SiO_2 insulating layer. The increase in I_{SD} with increasing $-V_G$ indicates that positive carriers are generated in the active Copoly-Non layer on the application of negative V_G, and the results agree with the electrochemical response of Copoly-Non which indicates that the polymer can generate positive carriers in electrochemical oxidation.[5] For evaluation of the mobility (μ) of the carrier in the active polymer layer, the following equation often used for polymer FETs[7e,8] is applied:

$$I_{SD}(\text{sat}) = (C_i W/(2L))\mu(V_G - V_t)^2$$

where I_{SD}(sat), C_i, W, L, μ, and V_t are the saturation current observed at a V_{SD} of -50 V, the capacitance of the insulating layer per unit (11 nFcm^{-2} for the present case), the channel width, the channel length (cf. the experimental part), the mobility, and the threshold voltage, respectively. Figure 3b exhibits the $I_{SD}(\text{sat})^{1/2}$ vs V_G plots, and the mobility μ is estimated at 2.5×10^{-3} cm^2 V^{-1} s^{-1} from the slope of the linear part where the electric current flows reasonably. Although we do not have regioirregular Copoly-Non at the moment, the regioirregular Copoly-Non, if it can be prepared, will not assume an aligned structure on the surface of the substrate, similar to the case of regioirregular P3RTh,[2c] and may give a lower mobility; this will be the subject of future investigation.

The obtained threshold voltage V_t of 16 V indicates that the application of plus voltage is necessary to obtain the off-state of the present FET; such a phenomenon is sometimes observed with polymer FETs. The on/off ratio is evaluated as approximately 200 from the log(I_{SD}(sat))$-V_G$ plots shown in Figure 3b.

Copoly-Pen yielded analogous polymer FETs and a similar μ. Because the electronic properties of such CT-type polymers can be tuned by various combinations of the donor and acceptor units, usability of the CT-type polymers in FETs will expand the scope of FETs.[9]

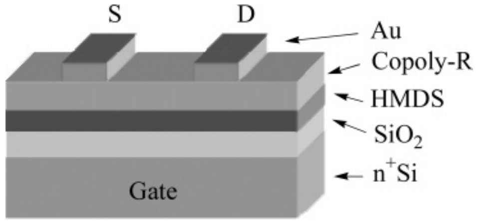

Figure 4. Schematic structure of the top contact Copoly-R FET used in this study.

Experimental Section

Materials and XRD Measurements. Copoly-R[5] and the copolymer of thiophene and 2-decylbenzimidazole[9] were prepared as previously reported. XRD patterns were recorded on a Philips PS-1051 and Rigaku RINT2000 instruments. Copoly-R films on a platinum plate were used for X-ray diffraction studies in the reflection mode at 40 kV and 40 mA with a scanning rate of 0.5° 2θ/min and Ni-filtered Cu Kα radiation from a 2-kW Rigaku X-ray generator. The cast films of Copoly-Pen and a chloroform-soluble fraction of Copoly-Non were prepared from trifluoroacetic acid and chloroform solutions, respectively, on a platinum plate, and dried under vacuum.

FET. The n-doped Si substrate having an oxide layer of 300 nm with a capacitance per unit area of 11 nFcm^{-2} was used as the gate of the FET. Trimethylsilyl functionalization of the Si/SiO$_2$ surface was carried out by exposing the silicon wafers to hexamethyldisilazane (HMDS) vapor in a closed container overnight. The Copoly-Non solution (chloroform-soluble fraction;[5] 0.5 wt % concentrated in chloroform) was spin-coated (1500 rpm) on the top surface of SiO$_2$ on the Si substrate. The organic semiconducting film was annealed for 24 h in a vacuum (10^{-2} Torr) at 60 °C. For the top contact geometry, gold electrodes forming channels of 250 μm wide (W) and 50 μm long (L) were thermally evaporated onto the semiconducting layer through a regular square-grid array shadow mask, and the device was fabricated as shown in Figure 4. FET measurements were performed under dry nitrogen atmosphere. Current$-$voltage characteristics were obtained with an Agilent 4155C semiconductor parameter analyzer.

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