



Mid-infrared characterization of thiophene-based thin polymer films[☆]



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ABSTRACT

Optical properties of seven regioregular poly(3-alkylthiophene) with different alkyl side chain lengths which are poly(3-butylthiophene-2,5-diyl) (P3BT), poly(3-pentylthiophene-2,5-diyl) (P3PT), poly(3-hexylthiophene-2,5-diyl) (P3HT), poly(3-heptylthiophene-2,5-diyl) (P3hept), poly(3-octylthiophene-2,5-diyl) (P3OT), poly(3-decylthiophene-2,5-diyl) (P3DT), and poly(3-dodecylthiophene-2,5-diyl) (P3DDT) have been studied in the mid-infrared (IR) spectral region by means of Fourier Transformation Infrared (FTIR) spectroscopy and IR spectroscopic ellipsometry (IRSE). Absorbance spectra obtained in this fingerprint region are potential to characterize the structures formed by organic molecules in thin films due to molecular vibrations in detail. In consequence, the vibrational absorption bands of these seven samples demonstrated that P3PT, P3HT, and P3hept exhibited very similar band profiles, in contrast, the stretching vibration of thiophene rings ($\approx 1465\text{ cm}^{-1}$; C=C) underwent a blue shift in P3BT, P3OT, P3DT and P3DDT. The highest value of the real part (ϵ_1) of the complex dielectric constant was obtained from P3HT on both indium thin oxide (ITO) and silicon (Si) substrates whereas the imaginary part (ϵ_2) was directly affected by increasing in the alkyl side chain lengths in a frequency range around 3000 cm^{-1} . The optical properties of P3PT in the mid-IR region developed an affinity with those of P3HT. Thus, P3PT is particularly a suitable polymer active material candidate for high-performance devices.

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1. Introduction

Thiophene-based conjugated semiconducting polymers such as regioregular P3ATs (P3BT, P3PT, P3HT, P3hept, P3OT, P3DT, and P3DDT) have been extensively studied for applications in optoelectronics such as organic field-effect transistors (OFET), organic light emitting diodes (OLED), and organic solar cells. One of the most well-known examples is P3HT as a *p*-type semiconductor material that has reached a charge carrier mobility of $0.1\text{ cm}^2/\text{V s}$ [1,2]. In order to improve the mobility of P3HT, investigations on molecular orientations [3,4], crystallization processes [5], various sorts of solvents for a wet process sample preparation [6], and the characteristic effects of doping [7] have been carried out so far. Furthermore, after different alkyl side chain lengths of P3ATs have been developed, correlation of physical and optical properties with the alkyl side chain ($\text{C}_n\text{H}_{2n+1}$) length was analyzed in detail. P3AT/PCBM blend investigations revealed that as the alkyl side chain increased, solubility increased as well as photocurrents in general [8]. Conversely, absorption coefficient reduced as the alkyl side chain length increased due to less interspace between molecules [8].

The hole mobility of P3ATs was determined by output characteristics [9]. In this study, P3HT indicated the highest hole mobility value ($1 \times 10^{-2}\text{ cm}^2/\text{V s}$) followed by P3BT ($1.2 \times 10^{-3}\text{ cm}^2/\text{V s}$), P3OT ($2.0 \times 10^{-4}\text{ cm}^2/\text{V s}$), P3DT ($6.6 \times 10^{-5}\text{ cm}^2/\text{V s}$), and P3DDT ($2.4 \times 10^{-4}\text{ cm}^2/\text{V s}$) in virtue of the superlative self-assembling ability. An even-odd effect in number of monomers has been confirmed in poly(phenylene ethynylene) (PPE) and poly(phenylenevinylene) systems [10], rigid-flexible polymers [11], and alkane thiol monolayers on gold [12]. These investigations revealed that the even-odd effect exceedingly influenced the transition temperatures, the molecular orientation angles, and the chain packing arrangements. Electrical properties of P3PT have been examined in UV and visible regions [13,14]. As a result, P3PT was presumed to be a possible candidate as a *p*-type semiconductor material since P3PT thin films exhibited a high degree of crystallinity with a π - π stacking distance, d_{010} of 3.74 \AA [14] which was very close to that of P3HT (3.8 \AA) [15].

In this paper, we examined the optical properties of seven regioregular P3ATs with alkyl side chain of $\text{C}_n\text{H}_{2n+1}$: $n = 4, 5, 6, 7, 8, 10, 12$ (P3BT, P3PT, P3HT, P3hept, P3OT, P3DT, and P3DDT), respectively, by means of FTIR spectroscopy in a frequency range between 800 and 3300 cm^{-1} . FTIR spectroscopy provides detailed information of each molecular bonding since absorption/transmission spectra represent the fingerprint of a material along with absorption peaks that are generated by vibrational transitions of atomic bonds. In addition, the dielectric properties of odd-num-

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bered P3hept and P3PT on Si and ITO substrates in the fingerprint region have been derived by the use of IRSE which is a technique that measures the variations in the polarization state of an incident light before and after reflection on a surface of a target material. Hereby accurate film thicknesses of thin films and their complex dielectric functions can be determined. The dielectric function of P3HT (even-numbered) has been derived as well in order to make a comparative study to odd-numbered materials. Moreover the surface roughness of all seven P3AT films was analyzed by atomic force microscopy (AFM).

2. Experiment

2.1. FTIR spectroscopy

FTIR spectrometers (Bruker IFS 66 v/S & Vertex 80 V) with a Deuterated Triglycine Sulfate (DTGS) detector were used for the measurements of IR spectra (absorbance) in a frequency range between 450 and 5500 cm^{-1} . All the absorbance measurements were carried out with a resolution of 4 cm^{-1} and a sample scan time of 1000 scans under a vacuum pressure between 2 and 5 mbar.

2.2. IRSE

ψ and Δ spectrum measurements were performed in a frequency range between 333 and 6000 cm^{-1} with an angle of incidence of 40°, 50°, 60°, and 70° under normal pressure by a rotating compensator IR ellipsometer from J. A. Woollam Co., Inc. (IR-VASE). In order to obtain the dielectric functions and the precise thickness of a thin film, ψ and Δ measured spectra were fitted based on an optical model by the use of WVASE32 software [37]. Fundamentally, these parameters are related to the Fresnel reflection coefficient r_p (p -polarized) and r_s (s -polarized) which determines the complex reflectance ratio ρ . Thus the complex reflectance ratio ρ can be described as:

$$\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan(\psi)e^{i\Delta} \quad (1)$$

where $\tan\psi$ denotes the relative amplitude attenuation while Δ represents the phase shift of the p and s linearly polarized components due to reflection.

Oscillations of atomic bonds are usually observed in the IR range due to a change in the dipole moment. The optical properties of an isotropic layer can then be expressed as a summation of Lorentzian oscillators

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_\infty + \sum_{j=1}^N \frac{s_j \omega_j^2}{\omega_j^2 - \omega^2 + i\gamma_j \omega} \quad (2)$$

where ε_1 is the real part of the dielectric function, ε_2 the imaginary part of the dielectric function, ε_∞ a real constant, N the number of oscillators, s_j an amplitude of the j th oscillator, γ_j the damping factor of the j th oscillator, ω_j the broadening parameter related to the j th oscillator, and ω the resonance frequency.

A film thickness can be determined by interferences between light reflected from different surfaces:

$$d = \beta \frac{\lambda}{2\pi \sqrt{N_2^2 - N_1^2 \sin^2(\phi_1)}} \quad (3)$$

where d is the film thickness, β the phase factor, λ the wavelength of light, N_1 the refractive index of surroundings, N_2 the refractive index of a film, and ϕ_1 the angle of incidence [16,17].

2.3. Sample preparation

We have acquired commercially available regioregular P3BT, P3PT, P3hept, P3OT, P3DT, and P3DDT from Rieke Metals Inc. [18], and P3HT (Lisicon SP001; molecular weight (MW) 43600 and regioregularity (RR \approx 95.9)) from Merck KGaA. It has been reported that solubility and field-effect mobilities of P3HT films were improved by dint of high boiling point (BT) solvents such as 1,2,4-Trichlorobenzene (BP: 213.5°) and 1,2-Dichlorobenzene (BP: 180°) due to progress of self-assembly [6,19]. Thus we selected 1,2-Dichlorobenzene (Merck KGaA) as a solvent for this investigation. Weight ratio percentage concentration of all the solutions was fixed to 2%. The solutions were placed on a hot plate with a temperature between 60 and 70 °C for 30 min so as to dissolve them thoroughly. All samples were prepared by spin coating process (SPS Europe: SPIN150-NPP) at rotation speed of 4000 rpm on Si wafers and ITO coated glass substrates (SiO_2 barrier coating was applied on polished soda lime float glass, and the ITO, resistance 7 Ω/sq , was deposited on it, VisionTek Systems Ltd. for both FTIR and IRSE measurements. As additional information, Drude metal modeling was employed for fitting the optical data of the ITO coated glass substrates.

3. Results and discussions

3.1. FTIR absorption spectroscopy

Absorbance spectra of P3BT, P3PT, P3hept, P3OT, P3DT, and P3DDT in the frequency range between 800 and 3300 cm^{-1} are shown in Fig. 1. Strong molecular absorption bands can be seen in the frequency range between 800 and 1600 cm^{-1} and 2800 and 3100 cm^{-1} . The films were fabricated nearly equivalent in thickness ($\approx 66 \pm 2$ nm) so as to compare the absorption strength of each sample. Table 1 summarizes the characteristic mid-IR bands of 7 materials, and the film thickness of each film is described in Table 2. The film thickness was determined by use of a Dektak (Veeco Dektak 150) and IRSE for Si and ITO substrates, respectively. The stretching vibrations of the thiophene rings were detected in the frequency range between 819 and 834 cm^{-1} [28]. The absorption peak around 1378 cm^{-1} was contributed by the methyl deformation [29]. The symmetric C=C stretching vibration bands of the thiophene rings were shown in the range between 1456 and 1467 cm^{-1} [28]. On the other hand, the antisymmetric C=C stretching vibration bands of the rings appeared around 1510 cm^{-1} [28]. These four absorption bands were related to the stretching vibration modes of the thiophene rings, and the symmetric C=C vibration band around 1465 cm^{-1} underwent a blue shift in P3BT, P3OT, P3DT and P3DDT compared with the P3PT, P3HT, and P3hept. In addition, P3PT was the one to show the strongest absorption peaks at 819 and 1456 cm^{-1} among all those 7 materials. Absorption peaks located between 2800 and 3000 cm^{-1} were contributed from the alkyl side chains. Absorptions around 2855 and 2925 cm^{-1} were caused by the symmetric and antisymmetric CH_2 stretching vibrations, respectively [30]. The antisymmetric CH_3 stretching vibration band took place around 2956 cm^{-1} [30] whereas the absorption peak around 3056 cm^{-1} was associated with the C–H stretching vibration band of the thiophene rings [28]. Systematic and unsystematic changes in the vibrational modes corresponding to the symmetric and antisymmetric CH_2 as well as the antisymmetric CH_3 were observed as the alkyl side chain length was varied as shown in Fig. 1. A systematic red¹ shift of both symmetric and antisymmetric CH_2 stretching

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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