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Assessment of the Intermolecular π–π Configurations of Poly(3-Hexylthiophene) using Polarized Raman Spectroscopy

Juwon Kim and Myeongkee Park*
Department of Chemistry, Pukyong National University, Busan 48513, Korea.
**E-mail: bikeplay@pknu.ac.kr*

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ABSTRACT. Precise molecular configuration elucidation of poly(3-hexylthiophene) (P3HT) through advanced spectroscopic techniques is pivotal for enhancing P3HT-based photovoltaic device efficiencies since its high charge-carrier mobility is directly correlated to its well-ordered structure. In this study, we examine Raman depolarization ratios of annealed and non-annealed P3HT films to elucidate their intermolecular π–π configurations. Our findings suggest that the backbone of the annealed film possesses stronger π–π conjugation overlaps than that of the non-annealed film owing to the greater depolarization ratio of the annealed film. In addition, the depolarization ratios are also supported by theoretical calculations, where parallel-stacked thiophene structures display a higher depolarization ratio compared with that of twisted-stacked structures, as calculated by the Møller–Plesset perturbation theory. This study highlights the utility of polarized Raman spectroscopy as a versatile tool for assessing the degree of molecular order in highly conjugated polymer films.

Key words: Poly(3-hexylthiophene), P3HT, Raman, Depolarization ratio, π–π overlap

INTRODUCTION

Poly(3-hexyl thiophene) (P3HT) is a conductive polymer extensively utilized in photovoltaic applications owing to its high charge-carrier mobility.[1-4] The enhanced electronic properties are derived from the intricate interplay of intra- and inter-molecular π-conjugated electrons within its ordered backbone structure, which is crucial for maximizing conductivity and photovoltaic efficiency.[2-7] Hence, elucidating precise molecular configurations using advanced spectroscopic techniques is essential for advancing our understanding of P3HT-based devices.[8,9]

A common strategy for inducing ordered structures in spin-coated P3HT films involves annealing at temperatures higher than 100 ℃, which has been studied using atomic force, scanning electron microscopy, and X-ray diffraction techniques.[10-13] In addition, Raman spectroscopy has been employed to investigate the detailed π-conjugated structures of P3HT at the molecular level, revealing small peak shifts and broadenings associated with structural variations.[14,15] However, elucidating the precise π-π stacked structures remains challenging because of the numerous structural conformations in P3HT (comprising over 200 mer units), leading to complexities in Raman spectral analysis. Thus, it is crucial to quickly analyze the overall Raman properties to understand and predict the molecular configurations.

Polarized Raman spectroscopy has been utilized to study the symmetry character of molecular vibrations. The Raman depolarization ratio ($\rho = I_{perpendicular}/I_{parallel}$) represents the ratio of Raman peak intensities measured using parallel- and perpendicular-polarized acquisitions. If a molecular vibration is highly polarized, it shows that the depolarization ratio is close to zero. In contrast, other vibrations that are 100% unpolarized exhibit a depolarization ratio of 1. Generally, if the depolarization ratio exceeds 0.75, the Raman mode is called an unpolarized band. In contrast, a polarized Raman mode shows $0 < \rho < 0.75$. For example, the ρ values of simple molecules, such as methane, typically show the range of 0–0.75, depending on the symmetry of the normal vibration mode of the molecule.[17] The depolarization ratio can also be utilized to study topological molecular orientation and facet information in complex systems.

Herein, we studied Raman of annealed and non-annealed P3HT films to compare their intermolecular π–π configurations. We also experimentally and theoretically conducted the polarized Raman spectroscopies, as a versatile tool for assessing the degree of molecular order in highly conjugated.

EXPERIMENTAL PROCEDURE

Sample Preparation

Regioregular (>99.0%) P3HT with a number average molecular weight (M_n) of 36,000–45,000 and a polydispersity index of 1.8 was purchased from TCI Incorporation. The product was used as received, without further purification. The P3HT solution was prepared in chlorobenzene (0.5% weight/volume) and spin-coated (2,000 rpm for 40 s) onto ozone–etched glass substrates in an N_2-filled glove box. The annealed P3HT film was fabricated by annealing at 120 ℃ for 10 min, and it was cooled to room temperature (approximately 22 ℃).

UV-Vis Absorbance and Raman Measurements

Absorption spectra were recorded using a UV-Vis spectrophotometer (V-770, JASCO). Raman signals were measured using a continuous-wave laser at 488 nm (LASOS60, Lambda Photometrics), an objective lens (25×, Nikon), a spectrograph (f = 500 mm, 1200 g/mm, Dongwoo Optron), and a CCD (iDus, Andor) (*Fig.* 1). For the polarized Raman measurements, a $\lambda/2$ waveplate (Newport Inc.), two Glan-Thompson polarizers (Newport Inc.), and a depolarizer (Thorlabs Co. Ltd.) were employed in the excitation and emission optical paths to cancel out the polarization effects. The laser power was reduced to approximately 2 mW using a variable neutral density filter (Thorlabs, Inc.) to avoid photobleaching. The power density was approximately 5 W/cm^2 at the sample position. The samples were continuously moved during Raman measurements using a one-dimensional translation stage to avoid photodamages. The signals were measured during 300 ms and integrated to 100 times. No significant changes in Raman intensity were observed during the measurements.

Theoretical Calculation

To simulate a real P3HT chain consisting of approximately 250 mer units, a cut-down P3HT analog containing eight hexylthiophene moieties was optimized and frequency-calculated using the B3LYP density functional theory (DFT) at the 6–31g(d,p) level. The calculated ground-state Raman frequencies were scaled using the vibration scaling parameter (0.961) at B3LYP/6-31g(d,p).[16] The depolarization ratios affected by intermolecular π-π interactions between P3HT chains were calculated using MP2 (Møller–Plesset perturbation, the second) theory at the 3–21g* level. We employed structure-optimization and frequency-calculation of Raman modes of two P3HT analogs composed of six thiophenes. In addition, to reduce the computational workloads, the hexyl groups of P3HT analogues were replaced with methyl groups. All calculations were performed using Gaussian 09 software.

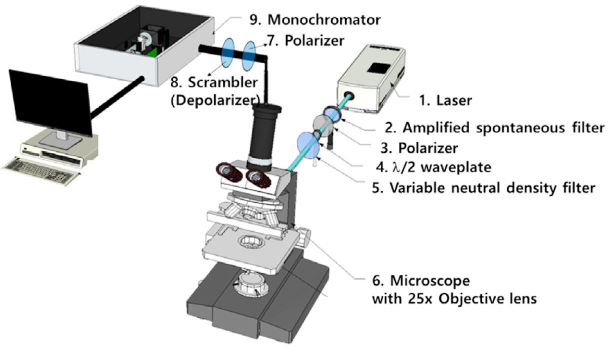

***Figure* 1.** Polarized Raman apparatus.

RESULTS AND DISCUSSION

Fig. 2a shows the UV-Vis absorbance spectra of the annealed and non-annealed P3HT films. The spectra exhibited the characteristic broad absorption edge of the P3HT films (~1.89 eV). There were no notable differences in the absorption band edges of the annealed and non-annealed films. The Raman spectra of the annealed and non-annealed P3HT films are shown in *Fig.* 1b. They commonly show characteristic C–C and C=C bond stretching modes of the thiophene ring at 1370 and 1450 cm^{-1}, respectively.[14] However, the Raman features of the films appear identical.

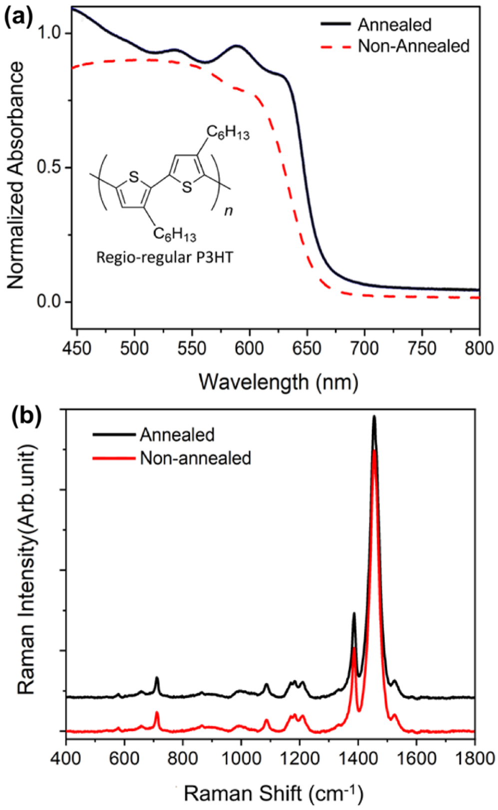

***Figure* 2.** (a) UV-Vis absorbance and (b) Raman spectra of annealed and non-annealed poly(3-hexylthiophene) (P3HT) films.

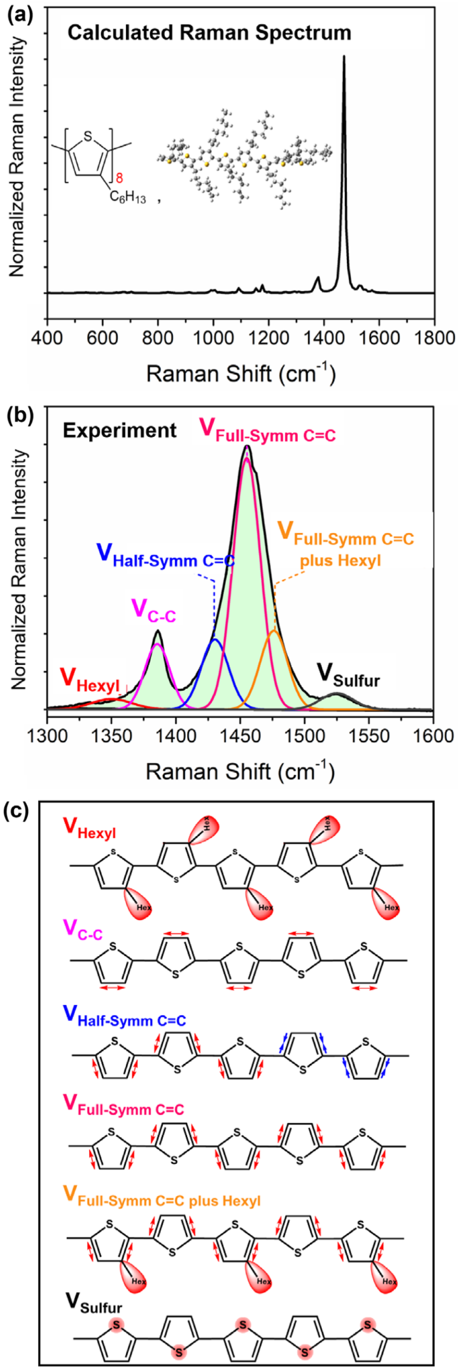

***Figure* 3.** (a) Calculated Raman spectrum of eight hexylthiophenes. (b) Measured Raman spectrum with peak assignments and (c) vibrational motions.

Thus, they rarely exhibit distinct Raman signatures upon annealing.

Hexylthiophenes are expected to exhibit at least six Raman-active vibrational modes of thiophene rings, excluding hydrogen-related vibrations. *Fig.* 3a displays the theoretical Raman modes calculated by DFT at the 6-31g(d,p) level, using a P3HT analog containing eight hexylthiophenes. The theoretical simulation successfully reproduces the experimental Raman results, with an intense Raman peak located at approximately 1480 cm^{-1} that is nearly identical to the experimental value of approximately 1450 cm^{-1}. Moreover, other smaller peaks are observed at frequencies similar to those in the experimental measurements. Consequently, we assigned the experimental Raman peaks to several theoretical vibrational Raman modes, as illustrated in *Fig.* 3b and c. The primary Raman peak located at 1450 cm^{-1} corresponds to a fully symmetric C=C stretching mode ($V_{\text{Full-Symm C=C}}$), which is accompanied by half-symmetric C=C stretching modes ($V_{\text{Half-Symm C=C}}$) and a $V_{\text{Full-Symm C=C}}$ for the hexyl group of a simple P3HT analog consisting of eight hexylthiophenes.

In other words, our simple Raman mode calculation indicates that, ideally, highly ordered P3HT exhibits a few intense Raman peaks for C=C stretching modes, which are easily distinguishable from the broadened Raman peaks of randomly disordered P3HT. However, a real P3HT film should contain individual or subgroup vibration modes for approximately 250 hexylthiophene rings in the case of P3HT (with a molecular weight of 40,000 Da). Moreover, the thiophene ring planes are not perfectly planar but are partially twisted because of the large steric effect of the hexyl groups. Thus, there are numerous C=C stretching modes that result in considerable Raman overlap at approximately 1450 cm^{-1}. This result was verified by Raman-mode calculations performed for a P3HT analog consisting of eight hexylthiophene rings. Thus, it can be challenging to detect Raman differences originating from ordered intermolecular π–π interactions using simple Raman spectroscopy.

We studied the polarized Raman spectra of annealed and non-annealed P3HT films, as shown in *Fig.* 4a and b, respectively. In our experiment, the depolarization ratios were measured to be 0.34 and 0.15 at 1450 cm^{-1} ($V_{\text{Full-SymmC=C}}$) for the annealed and non-annealed films, respectively. According to a previous report, C=C stretch is highly unpolarized, which show a high depolarization ratio of 0.42.[18] Our result shows the comparable depolarization ratio of 0.34 at C=C stretch, indicating the moderately unpolarized vibration found in more ordered thiophene rings. However, it was shown to be more polarized (with a lower depolarization ratio of 0.15) in the non-annealed film. The P3HT backbones expected to be highly structure- and morphology-entangled to each. We suggest that this entanglement can interfere the polarization character of the C=C stretch and lower the depolarization ratio of the vibration. Thus,

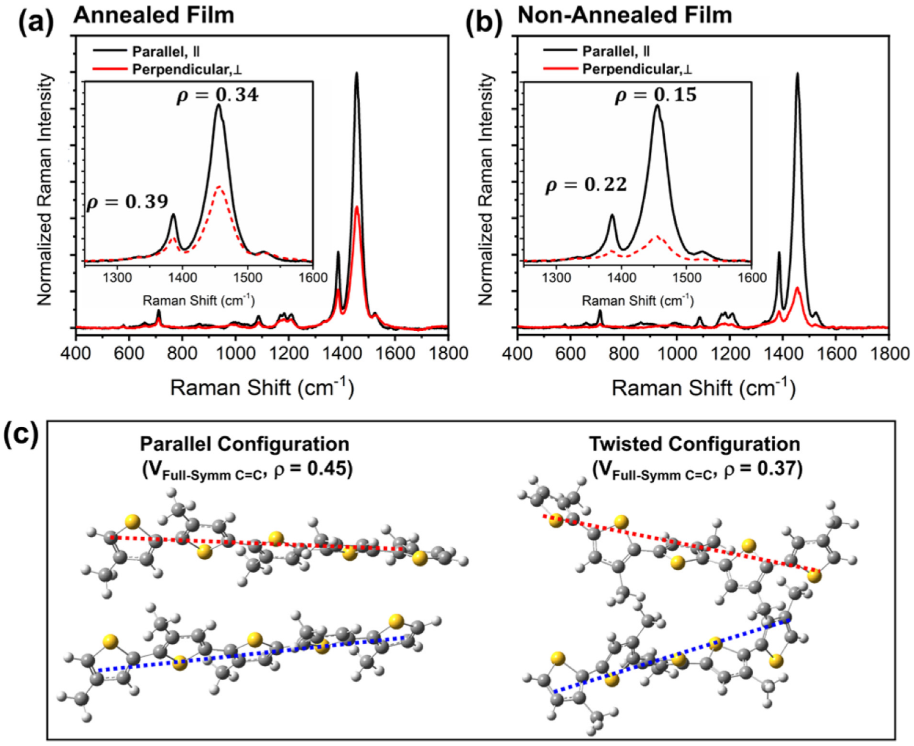

***Figure* 4.** Polarized Raman spectra and theoretically optimized stacked geometries. Polarized Raman spectra and depolarization ratios of (a) annealed and (b) non-annealed films measured with parallel (black solid line) and perpendicular (red dashed line) polarizations. (c) Optimized geometries for parallel and twisted structures, showing different depolarization ratios (ρ) of approximately 0.45 and 0.37 for the $V_{\text{Full-Symm C=C}}$ stretching mode, respectively.

the greater ρ value of 0.34 confirms that annealing induced more anisotropic and stronger intermolecular π–π conjugation in P3HT, resulting in more ordered π–π stacking. However, the lower value of 0.15 shows that more isotropic-disordered and entangled configurations were formed during room-temperature drying. In addition, it was determined that $V_{\text{C-C}}$ possessed a higher depolarization ratio (0.39) at 1380 cm^{-1} in the annealed film compared with that in the non-annealed film (0.22).

This result is also supported by the MP2 theory performed for the Raman mode calculations of the two chains composed of six thiophenes, which are parallelly and twisted located, respectively (*Fig.* 4c). Each backbone has six methyl groups instead of the hexyl moiety for cost-efficient computing.[19] The six methyl groups may not be enough to provide steric hindrance in backbones, However, in principle, the in-plane bulky hexyl group less interferes with the π–π interactions between the thiophene chain planes. Thus, methyl substitution does not seriously hurt the chemical information on the π–π interactions for two thiophene backbones.

We identified two distinct optimized structures that were parallel and twisted towards each other (*Fig.* 4c). The calculated Raman also showed intense C=C stretching Raman modes at approximately 1400 cm^{-1}, with depolarization ratios of 0.45 in the parallel configuration and a lower value of 0.37 in the twisted configuration. Thus, a more parallel configuration results in a higher depolarization ratio, which is more anisotropic. This observation strongly supports our polarization Raman spectra, which provides a good correlation between the Raman depolarization ratio and the extent of intermolecular π–π interaction.

CONCLUSIONS

We studied the Raman properties of annealed and non-annealed P3HT films using both experimental and theoretical methods. Our findings revealed that the annealed film exhibited a higher depolarization ratio than that of the non-annealed film, indicating a more ordered P3HT structure. These results suggest that depolarization ratio measurements can be used to assessing intermolecular interactions in thin conductive polymer films, particularly in cases where intermolecular π–π overlaps are crucial for charge carrier transportation in photovoltaic applications. Our future research will focus on studying depolarization ratios across various intermolecular π–conjugated polymer systems.

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