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Novel effects of compressed CO₂ molecules on structural ordering and charge transport in conjugated poly(3-hexylthiophene) thin films

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ABSTRACT

We report the effects of compressed CO₂ molecules as a novel plasticization agent for poly(3-hexylthiophene) (P3HT) conjugated polymer thin films. *In-situ* neutron reflectivity experiment demonstrated the excess sorption of CO₂ molecules in the P3HT thin films (about 40 nm in thickness) at low pressure ($P = 8.2$ MPa) under the isothermal condition of $T = 36$ °C, which is far below the polymer bulk melting point. The results evidenced that these CO₂ molecules accelerated the crystallization process of the polymer on the basis of *ex-situ* grazing incidence X-ray diffraction measurements after drying the films via rapid depressurization to atmospheric pressure: not only the out-of-plane lamellar ordering of the backbone chains but also intra-plane π - π stacking of the side chains were significantly improved, when compared to those in the control P3HT films subjected to conventional thermal annealing (at $T = 170$ °C). Electrical measurements elucidated that the CO₂-annealed P3HT thin films exhibited enhanced charge carrier mobility along with decreased background charge carrier concentration and trap density compared to those in the thermally annealed counterpart. This is attributed to the CO₂-induced increase in polymer chain mobility that can drive the detrapping of molecular oxygen and healing of conformational defects in the polymer thin film. Given the universality of the excess sorption of CO₂ regardless of the type of polymers, the present findings suggest that the CO₂ annealing near the critical point can be useful as a robust processing strategy for improving structural and electrical characteristics of other semiconducting conjugated polymers and related systems such as polymer: fullerene bulk heterojunction films.

INTRODUCTION

Conjugated polymers are of great scientific interest due to their potential for a variety of applications in organic electronic devices including solar cells¹⁻³ and field effect transistors (FETs)⁴⁻⁵. Poly(thiophene)s, such as poly(3-hexylthiophene) (P3HT), are one of the major cost-effective functional conducting polymer families that have been widely used, owing to their relatively high stability, high conductivity, and wide visible-light absorption.⁶⁻⁷ In the polymer-based organic devices, charge transport and optical properties strongly depend on molecular structures, chain orientations, and the degree of crystallinity in the active polymer layers, consequently affecting the overall device performances.^{5, 7-8} For example, enhanced charge carrier mobility and device performance can be achieved by improving molecular ordering and chain alignments of conjugated polymers, since charge transfer along the polymer backbone and π - π stacking direction are several orders of magnitude more efficient than that along insulating side chains.^{6-7,9} For this reason, the understanding of self-assembly processes in semicrystalline conducting polymer thin films, such as poly(thiophene)s, is of great value not only for fundamental polymer physics, but also for industrial applications as in organic electronic devices.

A spin-coating process is the most common way to prepare smooth and uniform conjugated polymer thin films for device fabrication. Resultant conjugated polymer films are confined between various interfaces, i.e., the polymer-air interface and the polymer-substrate interface. However, the fast solvent evaporation during the spin-coating process often leads to highly stressed and distorted chain conformations, which are far from their equilibrium. Various post-coating annealing procedures, including thermal and/or solvent annealing¹⁰⁻¹⁷, have been therefore required to achieve the optimized morphologies from the non-equilibrium poly(thiophene) or other π -conjugated spin-cast films in order to enhance their eventual device

performance. However, high temperature annealing above the bulk melting temperature (T_m) of high molecular weight P3HT ($T_m \sim 240$ °C, regioregular) may lead to a strong performance degradation in the P3HT-based device¹⁵⁻¹⁶. Although “mild” annealing at temperatures between T_m and the glass transition temperatures (T_g) of P3HT ($T_g \sim 10$ °C) can also facilitate the reorganization of P3HT crystals from the non-equilibrium state to more thermodynamically stable forms with improved crystalline ordering^{12, 18-19}, it often suffers from relatively low crystallinity and slow crystallization kinetics due to the limited chain mobility, subsequently affecting optical (light absorption) and electrical (charge mobility) properties in P3HT devices. While introducing solvent molecules in a polymer matrix as a plasticizer has shown a strong ability to enhance the chain mobility, crystallinity, and resulting charge transport properties in P3HT thin films^{5, 13, 20-22}, the use of organic solvents can raise environmental concerns. In addition, the crystallization of P3HT under solvent environment is complicated (which requires fine optimization of the volume ratio of added solvent, aging time, polymer concentration etc.), and the choice of solvents is extremely limited²³. Moreover, solvents can dissolve polymer chains or cause undesirable morphologies in spin-coated P3HT films, such as dewetting from substrates²⁴⁻²⁵. Hence, an alternative post-coating process for conjugated polymers is highly desirable for further development of polymer-based electronic devices.

Compressed CO₂ gas ($T_c = 31.1$ °C and $P_c = 7.38$ MPa) is one of the most promising “green” plasticization agents alternative to hazardous organic solvents.²⁶ In the case of thin film polymers, several groups have shown that the excess sorption of CO₂ molecules occurs near the critical point where the density fluctuations of CO₂ molecules becomes strongly correlated and maximum (known as the “density fluctuation ridge”²⁷ or the Widom line²⁸) regardless of the choice of polymers²⁹⁻³⁸. In general, the ridge emanates from the critical point, where the

amplitude of the density fluctuations diverges and separates the more liquid-like and more gas-like regions in the supercritical region^{27,39}. The vapor line below the critical point extends into the supercritical region due to a “memory effect”, and the extended line is called the ridge. This ridge is not specific to CO₂, but a general feature for other substances, such as H₂O, CF₃H, and Ar³⁹. It is also known that the ridge corresponds to a maximum or minimum of thermal conductivity⁴⁰, sound velocity⁴¹, and partial molar volumes⁴²⁻⁴³. In addition, the rate constants or equilibrium constants of various chemical reactions in supercritical fluids show maxima, minima or inflection points at the ridge⁴³. Interestingly, for polymer thin films subjected to the CO₂ treatment, it was found that the functional form of the anomalous swelling amplitude of the polymer exactly followed that of calculated density fluctuations in a pure CO₂ phase as functions of temperature and pressure²⁹⁻³⁰. Moreover, the plasticization effect associated with the excess CO₂ sorption can greatly enhance the chain mobility and crystallization kinetics of glassy/semicrystalline polymers by lowering their bulk T_g and T_m , especially at the vicinity of polymer air or polymer-solid interfaces^{29-31, 44-53}. Another unique feature of CO₂ annealing is ability to dry CO₂-exposed films via a rapid quench to atmospheric pressure without forming micron-sized voids⁴⁹.

In this article, we utilize compressed CO₂ gas near the critical point as a low-temperature, environmentally-friendly, and robust plasticization agent to improve the self-organization process of P3HT thin films. *In-situ* neutron reflectivity experiments demonstrated that the swelling isotherm of the P3HT thin film at $T = 36$ °C showed a maximum at the density fluctuation ridge (i.e., $P = 8.2$ MPa). We then characterized the CO₂-treated and subsequently dried P3HT thin films using *ex-situ* grazing incidence X-ray diffraction and atomic force microscopy techniques. The X-ray diffraction results showed that not only the out-of-plane

lamellar stacking but also the in-plane π - π stacking are improved simultaneously, resulting in a larger crystalline size in the CO₂-treated P3HT films compared to the P3HT films thermally-annealed at a higher temperature. We finally characterized the electrical properties of the CO₂-treated P3HT thin film and found that the CO₂ treatment increased the hole mobility in P3HT by ~500 % compared to the thermally annealed counterpart, while also decreasing the charge trap density and high background charge carrier concentration by similar magnitudes. These improvements in charge transport properties are attributed to the release of trapped oxygen molecules and associated charge traps from the P3HT film by CO₂ annealing, highlighting the potential of the CO₂ process for improving electrical performance of semicrystalline conducting polymers.

EXPERIMENTAL SECTION

Sample Preparation. Regioregular P3HT was purchased from American Dye Source Inc. with a number-average molecular mass of $M_n = 69$ kDa and an approximate regioregularity of 96 %. The T_g and T_m were determined to be 12 °C and 239 °C, respectively, by differential scanning calorimetry (DSC). Silicon (Si) substrates were first cleaned using ultrasonic treatment in detergent and acetone, and then subjected to an immersion in a hot piranha solution (i.e., a mixture of H₂SO₄ and H₂O₂, *caution: a piranha solution is highly corrosive upon contact with skin or eyes and is an explosion hazard when mixed with organic chemicals/materials; extreme care should be taken when handling it*) for 30 min, and were subsequently rinsed with deionized water thoroughly. The piranha solution-cleaned Si wafers were further immersed in an aqueous solution of hydrogen fluoride (HF) for 30 s to remove an oxide layer. X-ray reflectivity result showed that a thin oxide (SiO_x) layer of ~ 1 nm in thickness with a surface roughness of less than

0.3 nm was reproduced even after HF etching, possibly due to atmospheric oxygen and moisture, as reported previously⁵⁴. Thin P3HT films with a fixed thickness of approximately 40 nm were prepared onto the cleaned Si substrates by spin-coating from chlorobenzene solutions at room temperature with a rotation speed of 2500 rpm. The average thicknesses of the spin-cast P3HT thin films were measured with an ellipsometer (Rudolf Auto EL-II) with a fixed refractive index of 1.45. All the spin-coated P3HT films kept under vacuum (below 10^{-3} Torr) at 25 °C for 24 h before the CO₂ processing and the dried samples were then transferred into a high-pressure cell³⁰ immediately for CO₂ exposure. As will be discussed later, the neutron reflectivity experiments demonstrate that the CO₂ exposure at the density fluctuation ridge condition (i.e., $P = 8.2$ MPa and $T = 36$ °C)²⁷ for 24 h is satisfactory to achieve an improved ordered structure in P3HT. After the CO₂ exposure, the chamber was quenched to atmospheric pressure either rapidly with a quench rate of ca. 50 MPa/min (“rapid” quench), or slowly with a quenching rate of ca. 0.15 MPa/min (“slow” quench) to see whether the polymer crystalline structure is melted in CO₂, since the quench rates control the resulting morphology, as previously observed in poly(ethylene oxide) thin films⁵². As shown in Supporting Information (Figure S1), the grazing incidence x-ray diffraction results reveal no significant differences between the two quenching rates, implying the CO₂ treatment at the given pressure conditions up to 10 MPa does not melt the P3HT chains. Instead, the CO₂ molecules act as a plasticization agent^{50, 52, 55-56}, facilitating the crystallization process. For a comparison, we also treated the P3HT thin films via a conventional high temperature annealing at 170 °C for 24 h under vacuum ($\sim 10^{-3}$ Torr), followed by rapid quench to room temperature.

In-situ Neutron Reflectivity. With a large penetration depth, neutron reflectivity (NR) is an ideal tool to monitor the *in-situ* thickness, composition, and interfacial structure of polymer thin films immersed in fluids or gases, under high pressure in thick walled vessels^{30, 57}. The *in-situ* swelling behavior of the P3HT thin films in CO₂ was measured by NR. Approximately 40 nm-thick P3HT thin films were prepared on 3-inch Si wafers with identical cleaning and surface treatment as described above. Specular NR measurements were performed at the NG-7 reflectometer, National Institute of Standards and Technology Center for Neutron Research (NCNR). The wavelength (λ_N) of the neutron beam was 0.47 nm with $\Delta\lambda_N/\lambda_N = 2.5\%$. The details of the high-pressure NR experiments have been described elsewhere³⁰. The NR experiments were conducted under the isothermal condition ($T = 36\text{ }^\circ\text{C}$) with elevated pressures up to $P = 10.1\text{ MPa}$. Temperature and pressure stabilities during the NR measurements were controlled within an accuracy of $\pm 0.1\text{ }^\circ\text{C}$ and $\pm 0.2\%$, respectively. The P3HT thin films were exposed to CO₂ for up to 1 h prior to data acquisition. The scattering length density (*SLD*) values of CO₂, which vary from 0.0004×10^{-4} to $1.75 \times 10^{-4}\text{ nm}^{-2}$ in the pressure range of $0.1\text{ MPa} \leq P \leq 10.1\text{ MPa}$ at $T = 36\text{ }^\circ\text{C}$, were calculated based on the density of CO₂ obtained by the equation of state⁵⁸. The NR data was acquired by successively increasing pressure and then slowly decreasing pressure. Since the background scattering from a pure CO₂ phase increases dramatically near the critical point²⁹⁻³⁰, we measured the scattering from the pure fluid phase (i.e., the long-range density fluctuations) for the respective pressure condition. The NR data corrected for the background scattering was analyzed by comparing the observed reflectivity curves with the calculated ones based on model *SLD* profiles having three fitting parameters for each layer: film thickness, *SLD*, and roughness between the CO₂ and polymer layers represented as a

Gaussian function⁵⁹. It should be noted that we also included the thin SiO₂ layer of ~1 nm, which was determined by X-ray reflectivity, for the NR fitting.

Grazing Incidence X-ray Diffraction. Grazing incidence X-ray diffraction (GIXD) measurements for the CO₂-treated and thermally annealed P3HT thin films were carried out at the X9 beamline ($\lambda = 0.0918$ nm and $E = 13.5$ keV) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Two-dimensional scattering patterns were collected by using a MAR-CCD area detector. In order to see the differences in the microdomain structures between the topmost surface and the rest of the film, two different incident angles (α) were utilized: (i) $\alpha = 0.08^\circ$, which is just below the critical angle (α_c) of the total external reflection for P3HT ($\alpha_c = 0.12^\circ$) such that the electric field intensity decays exponentially into the film, and thereby scattering intensity is dominated by the surface area of ~ 10 nm depth; (ii) $\alpha = 0.16^\circ > \alpha_c$, where the X-ray penetration depth exceeds the film thickness such that we can obtain information on the average structures over the entire film. We denote the first experimental configuration as the “surface-mode” and the second one as the “film-mode” hereafter. All the experiments were carried out at room temperature under vacuum, and the exposure time for all the measurements was fixed to 300 sec.

X-ray Reflectivity Measurements. The specular X-ray reflectivity (XR) measurements were performed using an X-ray reflectometer (Bruker, D8 Advance) with Cu K α radiation at NCNR to study the expanded structures of the CO₂-treated P3HT film after depressurization. The wavelength (λ_x) of the X-ray beam was 0.154 nm with $\Delta\lambda_x/\lambda_x = 0.25$ %. The XR data corrected

for the background scattering was fitted using the ReFlpak software package⁶⁰ with a multilayer “slab” model for a *SLD* profile.

Atomic Force Microscopy Measurements. The surface morphologies of the CO₂-treated and thermally-annealed P3HT thin films were observed by atomic force microscopy (AFM) (Digital Nanoscope III and Bruker Bioscope Catalyst). A standard tapping mode was conducted in air using a cantilever with a frequency of 300 kHz and a spring constant of 40 N/m. The scan rate was 0.5 – 1.0 line/sec with scanning density of 512 lines per frame.

Device Electrical Measurements. For the electrical characterization, P3HT-chlorobenzene solutions were spin-cast (~ 40 nm in thickness) onto indium tin oxide (ITO)-glass substrates coated with 10 nm-thick MoO₃ hole transport layer deposited by thermal evaporation (Lesker PVD 75) at ~ 1×10⁻⁶ Torr. Each sample was then either thermally annealed or CO₂-treated as described earlier. Top 10 nm-thick MoO₃ transport layer and 100 nm-thick Au layer were then deposited on the processed P3HT film by thermal evaporation (at ~ 1×10⁻⁶ Torr) through a shadow mask (1 mm in diameter). Current density-voltage (*J-V*) characterization for the CO₂-treated and thermally-annealed P3HT films were performed by using an Agilent 4156C precision semiconductor parameter analyzer. The electrical properties were obtained by fitting *J-V* profiles to the space charge limited conduction model. For each sample, 3-5 devices were measured for statistics.

RESULTS AND DISCUSSION

Swelling experiments.

We start with the pressure-dependent swelling behavior of the P3HT thin film in CO₂ via *in-situ* NR measurements. Figure 1 (a) shows representative NR profiles for the P3HT film in CO₂ at four different pressures under the isothermal condition ($T = 36\text{ }^{\circ}\text{C}$): $P = 0.1\text{ MPa}$ (air), $P = 4.3\text{ MPa}$, $P = 8.2\text{ MPa}$, and $P = 10.1\text{ MPa}$. It should be noted that the contributions from the density fluctuations of the pure CO₂ phase (i.e., background) become significant near the ridge condition ($P = 8.2\text{ MPa}$ at $T = 36\text{ }^{\circ}\text{C}$) and overwhelm the observed intensity at $q_z > 0.06\text{ \AA}^{-1}$.^{29,48} The NR data corrected for the background scattering were fit by using the ReFlpak software package⁶⁰ with a multilayer “slab” model composed of the three fitting parameters for each layer. The thickness of the P3HT film, with the initial thickness of $43.6 \pm 0.4\text{ nm}$, gradually increases with increasing CO₂ pressure, until it reaches to the maximum value of $47.8 \pm 0.4\text{ nm}$ at $P = 8.2\text{ MPa}$, i.e., the density fluctuation ridge²⁹⁻³⁰. Figure 1 (b) shows the scattering length density (SLD) profiles of the P3HT obtained from the best fits. Since a simple boxlike shape profile could be approximated to represent the volume fraction profiles of the swollen P3HT film, it is reasonable to suppose that the solvent quality of CO₂ for P3HT is still poor⁶¹ even at the ridge condition. Figure 2 summarizes the linear dilation (S_f) of the 43 nm-thick P3HT film during the pressurization process. The S_f values were calculated by the equation, $S_f = (L_1 - L_0) / L_0$, where L_1 and L_0 are the measured thicknesses of the swollen and unswollen film, respectively. In the pressurization process, there is an anomalous peak in S_f near $P = 8.2\text{ MPa}$, which is attributed to the excess sorption of CO₂ molecules at the density fluctuation ridge, as previously reported²⁹⁻³⁸. It is postulated that the origin of the anomalous expansion is attributed to the formation of a large correlation hole around “CO₂-phobic” polymer chains (i.e., excluding the fluid molecules around the polymer chains). Within such solvation structures, the polymer chains are expanded as a thermodynamically stable state⁶²⁻⁶³. This expansion results in additional large solvent-density

fluctuations around the polymer chain over a larger area relative to the correlation length of the solvent molecules, thus lowering the free energy of the CO₂/polymer system⁶⁴.

To further investigate the swollen structure of the P3HT films in CO₂, the exposure time dependence of the swelling at the ridge condition ($T = 36$ °C and $P = 8.2$ MPa) was studied. As shown in Figure 2 (b), the S_f value gradually decreased from 0.096 ± 0.008 to 0.053 ± 0.008 during the CO₂ exposure, in contrast to a continuous increase in the SLD values of the P3HT/CO₂ mixture (SLD_{mix}) up to 18.5 h of CO₂ exposure. Note that the total mass of the P3HT/CO₂ mixture per unit area, which is proportional to $L_f \times SLD_{\text{mix}}$, remained almost constant as a function of exposure time. Since the S_f values decrease with increasing exposure time, the increase in the SLD value by 5 % during the course of CO₂ exposure (up to 22 h) is not attributed to the additional absorption of CO₂ molecules into the polymer matrix. Rather, this would be attributed to an increase in the density of P3HT film (i.e., the polymer chains become more crystallized) in the presence of the CO₂ plasticizer. This is further supported by the pressure dependence of the roughness (σ) at the polymer-CO₂ interface obtained from the best fits (Figure 2c). While the determination of σ near the ridge condition is difficult due to the high background scattering (i.e., the density fluctuations in the pure CO₂ phase), the roughness tends to increase with increasing pressure up to 10.1 MPa. This indicates that the CO₂ exposure at $T = 36$ °C does not induce the melting of the crystalline structures, which generally results in a much smoother surface, as previously reported in poly (ethylene oxide) thin films in CO₂⁵². Hence, the results overall support the CO₂-induced crystallization of the P3HT chains.

Investigation of Crystalline Phase.

Figure 3 shows representative the two-dimensional GIXD results of the 43 nm-thick P3HT films obtained at the surface and film modes after exposed to CO₂ at the ridge condition of 36 °C for 24 h. As seen from the figure, well-defined three-order diffraction peaks, consisting of primary (100), secondary (200), and tertiary (300) peaks, were observed along the out-of-plane direction (q_z -direction), while a strong (010) peak, which corresponds to the intraplane π - π stacking of P3HT chains, was observed in the in-plane (q_{xy}) direction. These GIXD results indicate the formation of a well-organized intraplane P3HT structure with lamellae oriented normal to the substrate surface (so called “edge-on” lamellae) during the CO₂ exposure within the entire film. Note that the edge-on lamellar orientation was observed in all the CO₂-treated P3HT films with different CO₂ pressures ($3 \text{ MPa} \leq P \leq 10.1 \text{ MPa}$) and different exposure times ($2 \text{ h} \leq t \leq 48 \text{ h}$), as well as in the thermal annealed films. We also confirmed that (i) no dewetting of the P3HT films occurs within at least 48 h of CO₂ treatment or thermal annealing in vacuum, and (ii) the CO₂-treated films after depressurization were stable for at least 1 month at room temperature and atmospheric pressure conditions. X-ray reflectivity results on the CO₂-treated P3HT films at the ridge condition of 36 °C are summarized in Figure S2 (Supporting Information).

Figure 4 shows the one-dimensional GIXD profiles along the q_z and q_{xy} directions under the surface and film modes for the P3HT thin film after CO₂ annealing at the ridge for 24 h. The scattering intensity was normalized by the penetration depth of the respective X-ray probed region for a comparison. It is clear that the multiple peak intensities from the topmost surface region are much higher than those of the entire film region, indicating that the backbone orientation or the lamellar stacking in the out-of-plane direction is much improved at the surface region. Moreover, the peak intensity of the in-plane (010) reflection at the surface region is about

4 times higher than that of the entire film, demonstrating the formation of more ordered π - π stacking at the topmost surface. These results are consistent with previous reports that show the anomalous CO₂ absorption into polymer thin films at the ridge condition is a surface effect due to the limited penetration power of the density fluctuating CO₂ molecules in a viscous polymer matrix^{29-30, 48-49, 65}.

To further elucidate the effect of CO₂ exposure on the P3HT structure, we fit the multiple peaks in the out-of-plane direction to a Gaussian function, determining the peak position (q_z^*) and peak width (β), which are related with the lattice constant (i.e., the intermolecular backbone distance, $a = 2\pi/q_z^*$),⁶⁶ and the average crystalline size (or the coherent length, $L = (0.9\lambda)/(\beta\cos\theta)$, with scattering angle θ)⁶⁷. We found that the lattice constant of the CO₂-treated P3HT film after 24 h CO₂ exposure at the ridge slightly decreased to $a = 1.60 \pm 0.01$ nm, which is smaller than that of the thermally annealed film at 170 °C for 24 h ($a = 1.64 \pm 0.01$ nm). This result implies that the thiophene backbones or the lamellar stacking in the CO₂-treated film is more compactly packed than that of the thermally-annealed film. In addition, the L value of the CO₂-treated film (at the ridge for 24 h) was estimated to be $L = 12.4 \pm 0.5$ nm, which is also greater than that of the thermally annealed film ($L = 9.1 \pm 0.5$ nm) (Figure 5a), again showing that CO₂ treatment results in a more highly ordered P3HT crystalline structure compared to the thermal annealing. Consistently, the (010) peak is also intensified after 24 h exposure of CO₂ at the ridge condition compared to the thermally-annealed film, indicating a much improved intraplane π - π stacking after the CO₂ process. These results suggest that the CO₂ annealing at the ridge plays a crucial role as an effective plasticization agent to enhance the polymer chain mobility and hence prompt the reorganization of the P3HT crystalline structures in both the out-of-plane and in-plane directions simultaneously. Given the lesser degree of structural reorganization observed in the

thermally-annealed P3HT film despite its much higher processing temperature (170 °C) than the CO₂ treatment ($T = 36$ °C) with a same annealing time (24 h), it is clear that the low-temperature CO₂-annealing is much more effective in enhancing the crystalline order of P3HT thin films than conventional thermal annealing even when the process condition is far below the bulk T_m .

AFM was used to further investigate the effect of CO₂ annealing on the surface morphology of the P3HT thin films. Figure 6 shows the AFM height images of both the CO₂-treated P3HT film at the ridge for 24 h and the thermally-annealed P3HT film ($T = 170$ °C for 24 h). As a comparison purpose, the as-cast P3HT film is also shown in the figure. As seen from the images, the surface of the as-cast P3HT film is featureless with a surface root-mean-square (RMS) roughness of $\sigma_q = 2.6$ nm, which is in line with previous report⁶⁸. At the same time, nanoribbon-like structures are found in the phase images (see, Figure S3 in Supporting Information), which are attributed to the long-range lateral ordering of P3HT crystals⁶⁸⁻⁶⁹. After the as-cast film was thermally annealed at 170 °C for 24 h, the surface RMS roughness increased to $\sigma_q = 6.1$ nm due to the surface aggregation of the P3HT molecules into disk-type granular crystals (edge-on lamellae) (Figure 6 (b)). On the other hand, it was found that similar disk-type granular crystals were also formed after the CO₂ annealing, but, with much more increased surface RMS roughness, as high as $\sigma_q = 10.8$ nm. This again suggests that the CO₂ annealing is more effective in promoting larger P3HT crystalline aggregates with enhanced molecular ordering than the conventional thermal annealing.

Electrical measurements.

Finally, we discuss the effects of the improved stacking of P3HT chains on electrical properties. Hole-only charge transport properties were examined by measuring current density -

voltage (J - V) characteristics of the processed P3HT thin films sandwiched between bottom indium tin oxide (ITO)/MoO₃ and top MoO₃/Au electrodes. Figure 7 shows the representative J - V characteristics of the thermally-annealed and CO₂-treated P3HT devices under dark ambient conditions (top). From the figure, it is apparent that the CO₂-treated P3HT at the ridge condition for 24 h shows more pronounced non-linear J - V characteristic with increased conductance compared with the thermally annealed (24 h at 170 °C) P3HT film. The corresponding double logarithmic plot (Figure 7 bottom) reveals that the thermally-annealed P3HT film largely follows the Ohmic conduction (i.e., slope ~ 1) within 2 V bias range, while the CO₂-treated film displays a transition from the Ohmic to space charge limited conduction (SCLC, slope ~ 2) with transitioning voltage (V_{Th}) ~ 0.3 V. The conduction in the thermally-annealed P3HT film started deviating from the Ohmic behavior for $V > \sim 3$ V range (i.e., $V_{Th} > 3$ V) but did not fully converge to SCLC (data not shown), indicating a much larger background charge carrier density.⁷⁰⁻⁷² The Mott-Gurney equation predicts that under the SCLC (either trap-free or with fully filled traps), J increases quadratically with V with following relation:⁷⁰

$$J = 98 \epsilon_0 \epsilon_r \mu V^2 d^3 \quad , \quad (2)$$

where μ is the charge carrier mobility, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant of the semiconductor (~ 3 for P3HT), and d is the thickness of the semiconductor layer. From the SCLC-dominated bias region in Figure 7, we find that the hole mobility of the P3HT film CO₂-treated at the ridge condition is enhanced to $\sim 3 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, compared with $\sim 0.6 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the thermally-annealed counterpart (Table 1). The mobility in the thermally-annealed P3HT was estimated from the lower-bound background carrier density corresponding to $V_{Th} = 3$ V and the measured Ohmic conductivity (σ) for $V < 3$ V via the following relation:⁷¹⁻⁷²

$$\mu = 89 d^2 \epsilon_0 \epsilon_r \sigma V_{Th} \quad (3)$$

The higher hole mobility in the CO₂-annealed P3HT compared with the thermally annealed sample can be attributed to the improved structural order in P3HT after the CO₂ processing, as discussed in the aforementioned NR and GIXD results that are consistent with previous studies reported by Kokubo and Yang⁷³, who showed that the CO₂-induced polymer chain mobility promoted a higher-order self-assembled structures in P3HT polymers. It should be emphasized that their CO₂ process condition ($T = 20\text{ }^{\circ}\text{C}$ and $P = 4.8\text{ MPa}$) is not as effective as our ridge condition so that their CO₂ exposure times were extended up to 96 h. It is noted that in our study the hole mobility enhancement was also accompanied by a near one order of magnitude reduction in charge carrier density (n) to $\sim 7 \times 10^{16}\text{ cm}^{-3}$ of the CO₂-treated P3HT film from $\sim 3 \times 10^{17}\text{ cm}^{-3}$ of the thermally annealed P3HT film, where n was evaluated based on its relation to the threshold voltage (V_{th}) over which the low-bias Ohmic conduction was transitioning to SCLC as the contact-injected excess charge carriers started overwhelming the pre-existing background charge carriers.⁷²

$$n = 98\epsilon_0\epsilon_r e V_{th} d^2 \quad (4)$$

with e being an elementary charge. Given the ambient air handling of our samples, molecular oxygen is expected to be responsible for the p-type doping of P3HT and the increased background charge carrier density—oxygen molecules are known to interact with the thiophene rings in P3HT, affecting the charge carrier density as well as hole mobility through the charge transfer mechanism⁷⁴⁻⁷⁵. The decrease in the oxygen doping amount in P3HT as indicated by the reduced V_{th} ^{72, 76-77} suggests that the CO₂-induced higher polymer chain mobility allowed a more efficient release of oxygen molecules from the P3HT film.

We also found that the CO₂-treated P3HT film exhibits a lowered charge trap density (N_T) compared with the thermally annealed counterpart. N_T was estimated by fitting the high bias

region of J - V characteristics (Figure 8) to the Poole conduction model, where the charge transport is mediated by the continuous trapping and detrapping events of charge carriers among the closely spaced, adjacent trap sites, resulting in the following J - V relation:^{71, 78}

$$J \propto \exp(eS2kTVd) \quad (5)$$

with k being the Boltzmann constant and S the inter-trap spacing which is directly related to N_T ($N_T = S^{-3}$). As summarized in Table 1, N_T in the CO₂ treated P3HT film is $\sim 2.4 \times 10^{21} \text{ cm}^{-3}$, nearly one order of magnitude lower than that observed in the thermally-annealed P3HT film ($\sim 1.6 \times 10^{22} \text{ cm}^{-3}$). In the case of organic semiconductor thin films, the existence of trap states localized in the bandgap was well documented^{22, 79}, and the structural and morphological defects, disorders, and impurities are typically responsible for the formation of charge traps.^{71, 80} The significantly lower N_T value in the CO₂-treated film again indicates that the CO₂ process induces a more significant polymer chain mobility compared with the thermal annealing, more efficiently remedying conformational disorders in polymers, as well as releasing molecular oxygen, both of which are known to be able to create charge traps.

CONCLUSION

We have investigated the effects of CO₂ annealing near the critical point on the chain stacking structures in the spin-cast P3HT thin films. *In-situ* NR measurements revealed the excess sorption of CO₂ molecules in the P3HT thin film at $T = 36 \text{ }^\circ\text{C}$ and $P = 8.2 \text{ MPa}$, where the density fluctuations of CO₂ become maximized. In addition, the NR data indicates that the CO₂ molecules expedite the crystallization process rather than the melting of the crystalline structures. In order to further clarify the plasticization effect associated with the excess CO₂ sorption on the crystalline structures, *ex-situ* GIXD and AFM experiments were performed after drying the films

via rapid depressurization process. The results are intriguing to exhibit more enhanced out-of-plane lamellar stacking as well as the in-plane π - π stacking along with a larger crystal size, when compared to the thermally-annealed P3HT counterpart. These results demonstrate that the CO₂ near the critical point acts as a robust plasticization agent, significantly enhancing the polymer chain mobility and, therefore, improving the molecular ordering of polymer chains even at the temperature far below the bulk melting temperature. Electrical measurements further showed that the CO₂-annealed P3HT films exhibited largely enhanced charge carrier mobility as well as decreased charge trap and background carrier densities, compared to the P3HT films subjected to thermal annealing. We postulate that these improvements in the electrical performance are attributed not only to the better crystalline ordering of the CO₂-annealed P3HT films but also to the higher efficiency in alleviating trapped oxygen molecules and charge traps from the P3HT film due to the enhanced polymer chain mobility. Since CO₂ is non-toxic and environmentally benign, and the excess sorption of CO₂ molecules in polymer thin film is rather general regardless of the choice of polymers²⁹⁻³⁸, the use of compressed CO₂ gas as a plasticization agent can be a robust, green processing method for improving the structural ordering and charge transport properties in conjugated polymer thin films used in organic electronic devices. Along the line, we are currently conducting the studies on the effect of the same CO₂ annealing on conjugated polymer:fullerene bulk heterojunction films, and the summary will be reported in the near future.

FIGURES

Figure 1. (a) NR profiles for the original 43 nm thick P3HT film at the four different pressures and $T = 36$ °C. The solid lines correspond to the best fits to the data based on the corresponding *SLD* profiles shown in (b).

Figure 2. (a) S_f of the P3HT thin film as a function of pressure at the density fluctuation ridge ($T = 36\text{ }^{\circ}\text{C}$ and $P = 8.2\text{ MPa}$). The open circles correspond to the S_f in the pressurization process, while the solid triangles correspond to the S_f in the depressurization process. (b) CO_2 exposure time dependence of S_f and SLD of the P3HT thin film at the density fluctuation ridge. (c) Full width at half maximum (FWHM) roughness as a function of pressure at $T = 36\text{ }^{\circ}\text{C}$.

Figure 3. 2D GIXD images for the CO₂-treated P3HT thin film (the original thickness of 43 nm) after CO₂ expose at the ridge for 24 h: (top) surface mode; (bottom) film mode with the same accumulation time (300 sec).

Figure 4. GIXD profiles of the P3HT thin film (the original thickness was 43 nm) along (top) the q_z and (bottom) q_{xy} directions after the CO_2 annealing at the ridge condition.

Figure 5. GIXD profiles of the P3HT thin film (the original thickness was 43 nm) along (top) the q_z and (bottom) q_{xy} directions after the CO_2 annealing at the ridge condition.

Figure 6. AFM height images of the 43 nm-thick P3HT films after (a) spin-casting, (b) thermally annealed at $T = 170\text{ }^{\circ}\text{C}$ for 24 h and (c) exposing to CO_2 at the ridge condition for 24 h. The height scales of all the images are 0 - 40 nm. The corresponding cross-sectional height profiles of the images with larger scale are shown in (d).

Figure 7. Representative J - V characteristics of thermally-annealed and CO_2 -treated P3HT hole only devices, with top panel showing a linear plot and bottom a double-logarithmic plot. Dashed lines indicates regions dominated by Ohmic conduction ($V < \sim 0.3$ V) and SCLC ($V > \sim 0.3$ V), respectively.

Figure 8. Representative semi-logarithmic J - V characteristics of thermally-annealed and scCO_2 -treated P3HT hole only devices, indicating high bias linear regions fitted to the Poole conduction model.

Table 1. Summary of charge transport parameters obtained from the analysis of J - V characteristics.

Post-process	m [$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$]	n [cm^{-3}]	S [nm]	N_T [cm^{-3}]
Thermal	6.3×10^{-6}	3.5×10^{17}	0.39	1.6×10^{22}
CO ₂ treatment	3.0×10^{-5}	7.0×10^{16}	0.75	2.4×10^{21}

Supporting Information. The effect of CO₂ quenching rates on the P3HT structures, X-ray reflectivity results before and after CO₂ exposure, atomic force microscopy phase image of the P3HT film after exposing to CO₂. This material is available free of charge on the ACS Publications website at DOI: xxx/xxxx

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Notes

The authors declare no competing financial interest.

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