864 *Chem. Mater.* **1994,** *6,* 864–870

Effects of Heat Treatment on Properties of Poly(3-alkylthiophene)

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Received December 3, 1993. Revised Manuscript Received February 28, 1994⊗

Structural, optical, and electrical properties of poly(3-dodecylthiophene) (P3DT) at room temperature have been studied after heat treatments at various temperatures. The crystallinity and the size of the crystallite of P3DT increased after the heat treatment, and the intensity of photoluminescence and the bandgap energy decreased. The electrical conductivity decreased with increasing the heating temperature, while the lattice parameter *a* decreased but the lattice parameter *b* increased. These results suggest that the interchain hopping of charge carrier between neighboring π-conjugation planes is the dominant process in the conductivity and carrier mobility of P3DT. The effects of higher order structure such as crystallinity and the conformation of main chain on electrical and optical properties are discussed.

Introduction

Conducting polymers having a conjugated π-electron system in the main chain have attracted much attention in recent years from fundamental and practical viewpoints.[1-5] The conducting polymers change their properties such as conductivity and color upon doping. In the neutral state, the conducting polymers show electronic and optical properties as a semiconductor, while metallike properties are observed in the doped state. These characteristic behaviors have been interpreted in terms of formation of soliton, polaron, and bipolaron upon doping,[1-3] which has stimulated practical studies and synthesis of various novel functional conducting polymers.

Among various conducting polymers, poly(3-alkylthiophene) (P3AT, shown in Figure 1) is the most interesting one because of its characteristic properties such as solubility for various organic solvents, fusibility at relatively low temperature, gel characteristics, solvatochromism, and thermochromism.[6-9] The authors have studied fundamental properties of P3ATs with various alkyl side groups and have proposed a number of functional applications such as battery, FET, light-emitting device, and photocatalyst.[10-14]

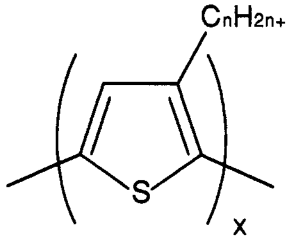

Figure 1. Molecular structure of P3AT.

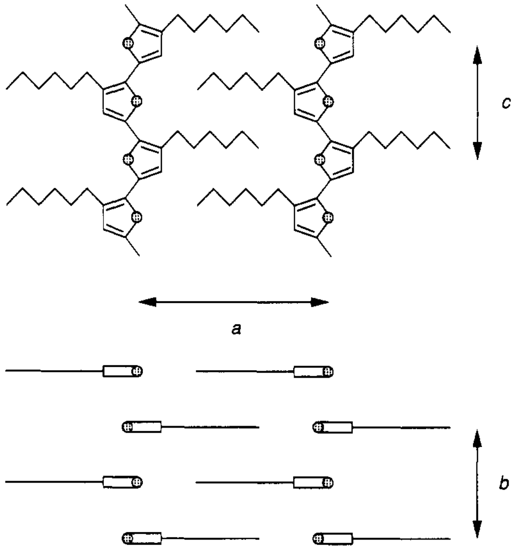

Figure 2. Orthorhombic crystal structure of P3AT.

Recently, Tashiro et al. have studied the crystal lattice of P3ATs with various alkyl side chains using uniaxially oriented films and have reported that P3ATs with alkyl chains shorter than 12 have an orthorhombic lattice structure as shown in Figure 2,[15] though a different structure has been proposed on a basis of X-ray powder diffraction measurements of nonoriented samples.[16] The

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⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1994.

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trans–gauche conformational isomerization was observed by FT-IR measurements in the side alkyl groups upon heating, which is thought to cause the conformational change of main chain and to result in the change in bandgap energy, that is, the thermochromism of P3AT.[8] The FT-IR analyses have confirmed the chemical structure of Figure 1.[15] Some endothermal peaks were observed in DSC measurements upon heating in the temperature region of the premelting and the melting points.[10,15]

We have also found in P3ATs that the conductivity shows a unique temperature dependence and thermal relaxation after a heating–cooling cycle.[17] Tashiro et al. have also found anomalous hysteresis in the DSC measurements upon heating–cooling cycles.[15] The origin of these phenomena should be clarified through detailed analysises of thermal effects on higher order structures such as crystallinity, lattice parameters, conformation of the side chain and coplanarity of π-conjugation plane of the main chain of P3ATs.

In the present study, the effects of the heat treatment upon the electronic and optical properties of neutral poly(3-dodecylthiophene) (P3DT) having alkyl chain length of 12 are studied in detail and discussed in terms of changes in higher order structure.

Experimental Section

The monomer used in the preparation of the sample polymer has been provided from Tokyo-Chem. Ind. The P3DT used in this study was obtained by the chemical polymerization of 3-dodecylthiophene with $FeCl_3$ as a catalyst.[18]

The typical polymerization procedure is as follows: 20 mL of chloroform solution containing 0.01 mol of the monomer was added slowly to the 100 mL of chloroform solution containing 0.04 mol of dried $FeCl_3$ under the argon atmosphere. The solvent was dried prior to use. The reaction was stopped after 2 h by mixing the reaction mixture with methanol and the precipitate was collected on a Buchner funnel followed by washing with methanol. The powder was washed with methanol by the Soxhlet extraction under argon atmosphere for 2 days. P3DT, which is soluble in chloroform, was obtained by extraction with chloroform. After repetitive reprecipitations with chloroform–methanol system, the soluble P3DT was obtained as a deep-red powder. Elemental analysis showed good agreement with the calculated elemental composition of $(C_{16}H_{26}S)_n$. The molecular weight (M_n) of the sample prepared by the same method has been reported to be about 2.1×10^4.[10] Leclerc et al. have studied the chemical structure of poly(3-alkylthiophene) prepared by a similar method and reported that most of the thiophene rings (>80%) coupled together in a head-to-tail structure.[9] They have also reported similar molecular weights ($M_n = 2.6 \times 10^4$) to our results.

The obtained polymer was casted from chloroform solution to form a thin film on a glass plate and an In–Sn–oxide (ITO) coated glass plate. The P3DT films were evacuated for 2 h at room temperature to remove residual chloroform and heated for 3 h at various temperatures for annealing in order to obtain the samples with different crystallinity. Then the samples were cooled down slowly with the cooling rate of 30 °C/h. These heat-treatment procedures were performed under the vacuum.

Right after the samples were cooled down to room temperature, measurements were performed as follows: X-ray diffraction measurements were performed in the reflection mode by utilizing Rigaku RINT-1100 system with the Cu Kα line of 1.54 Å in wavelength. UV–visible absorption spectra and photoluminescence were measured by utilizing a Hitachi 330 spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer, respectively. The electrical measurements were carried out using standard two-probe technique in an evacuated chamber. The ESR spectra were studied by using a Bruker ESP 300 spectrometer at X-band (9.5GHz) with low microwave power (200 μW). The Fourier transform infrared (FT-IR) spectra were measured by use of a JASCO FT/IR-3 Fourier transform infrared spectrometer. All these measurements were performed at room temperature.

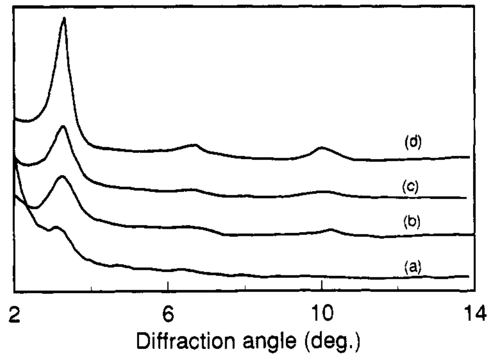

Figure 3. X-ray diffraction spectra of P3DT. The temperature of the heat treatment is (a–d, bottom to top) (a) before heat, (b) 50 °C, (c) 90 °C, and (d) 120 °C.

Results and Discussion

To investigate the changes in the crystallinity and the crystal structure of P3DT upon heat treatment, the X-ray diffraction measurements were performed. Figure 3 shows the X-ray diffraction spectra of P3DT films measured at room temperature right after the heat treatment at different temperatures. No peak disappeared and also newly appeared upon heat treatment. Therefore, the orthorhombic crystal structure should be maintained after the heat treatment. The intensity of (100) peak at about 3° increased with increasing temperature (T_h) of the heat treatment, while the fwhm (full width at half-maximum) of the peak gradually decreased. Other (h00) peaks, such as (200) peak at about 6.7° and (300) peak at about 10.0°, changed similarly to the (100) peak as seen in Figure 3. This spectral change means growth of the crystal region and the size of the crystallite in the P3DT films with heat treatments. The size of the crystallite can be estimated by the fwhm of each (100) peaks by using Scherrer's equation:

$$D_{hkl} = K\lambda/\beta \cos \theta \tag{1}$$

where D_{hkl}, K, λ, β, and θ are size of crystallite normal to the (hkl) plane, constant of 0.9, wavelength of X-ray, fwhm of (hkl) peak, and diffraction angle, respectively.[19] The D_{100} values evaluated from eq 1 are plotted in Figure 4a. With increasing temperature of heat treatment, the D_{100} value increased from ca. 100 to ca. 300 Å.

The crystallinity was evaluated using eqs 2 and 3 as follows:[20,21]

$$\frac{I_c}{I_{100c}} + \frac{I_a}{I_{100a}} = 1 \tag{2}$$

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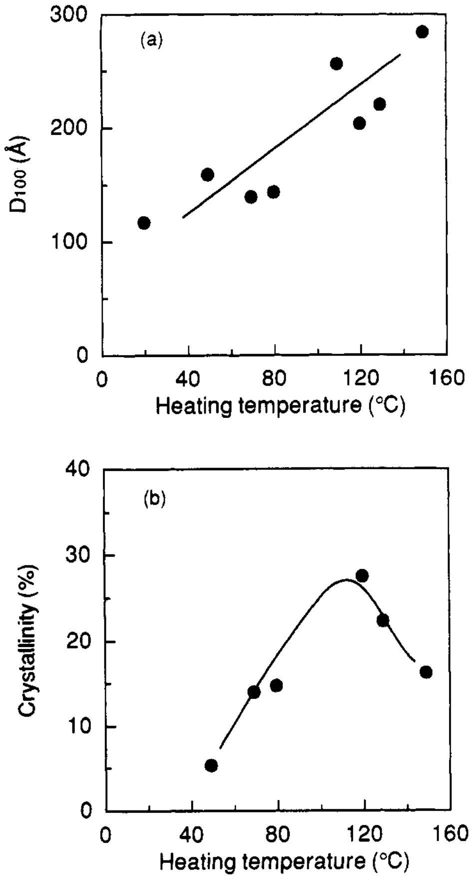

Figure 4. Plots of the size of crystallite (D_{100}) and crystallinity against the heating temperature of the heat treatment.

where I_c and I_a are integrated intensities of X-ray scattered by crystalline and amorphous region of the partially crystalline specimen, respectively. To plot the values of I_c against I_a of various samples, the regression line (eq 2) is obtained. I_{c100} which is integrated intensities of hypothetically prepared 100% crystallinity sample can be evaluated from the crossing point of the regression line with the I_c axis. Similarly I_{a100} which is the integrated intensity of 100% amorphous sample is obtained from the crossing point of the regression line with the I_a axis. The crystallinity (x_c) can be measured along this regression line as indicated by the eq 3.

$$x_c = \frac{1}{1 + KR}, \quad R = \frac{I_a}{I_c}, \quad K = \frac{I_{100c}}{I_{100a}} \qquad (3)$$

In the case of neutral P3DT, the value of K is evaluated to be 0.512 by using the integrated intensities of (h00) peaks. Figure 4b shows the changes in the crystallinity of P3DT films after the heat treatments evaluated from the eq 3.

As shown in this figure, the crystallinity increased with increasing the heating temperature and decreased above 120 °C. These enhancements of crystallinity were thought to be caused by the annealing at the temperature below the melting point. The crystallinity can be controlled and increased up to 30% by choosing the conditions of the heat treatment.

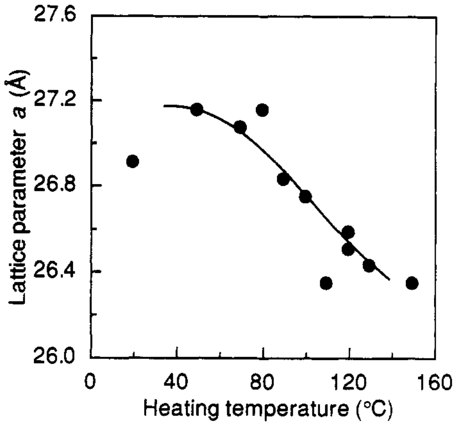

Figure 5. Plots of the lattice parameter a against the temperature of the heat treatment.

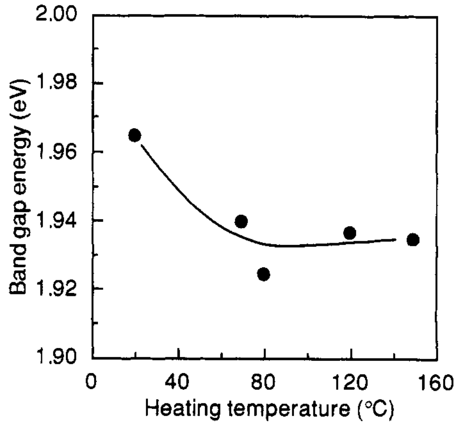

Figure 6. Bandgap energy of P3DT after the heat treatment.

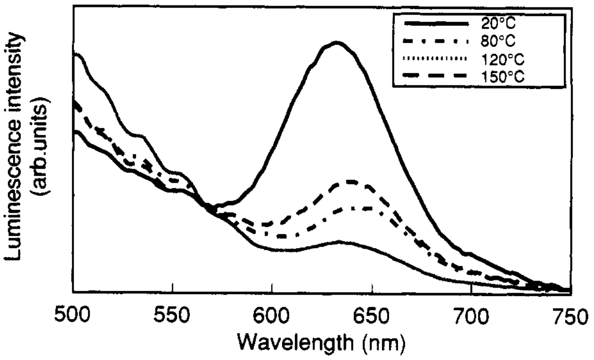

Figure 7. Photoluminescence spectra of P3DT with various temperatures of the heat treatments.

The lattice parameter a evaluated from the (100) peak decreased with increasing of the heating temperature as shown in Figure 5. This structural change seems to be originated in the reduction of the steric hindrance in the growth of the crystal region and the enhancement of the crystallinity upon heat treatment. Consequently the main chains are packed denser than before heating, resulting in a decrease of lattice parameter a.

To investigate the effects of crystal structures on optical properties, absorption spectra and photoluminescence measurements were performed. Though no marked change in the shape of absorption spectra was observed after the heat treatment, the bandgap energy evaluated from the threshold wavelength of the absorption due to the interband excitation decreased by the heat treatment, tending to saturate as shown in Figure 6. Figure 7 indicates photoluminescence spectra of P3DT film measured at room temperature after the heat treatment at various temperatures. It should be noted in this figure that with increasing temperature, the emission peak corresponding to radiative recombination of the excitons on the main

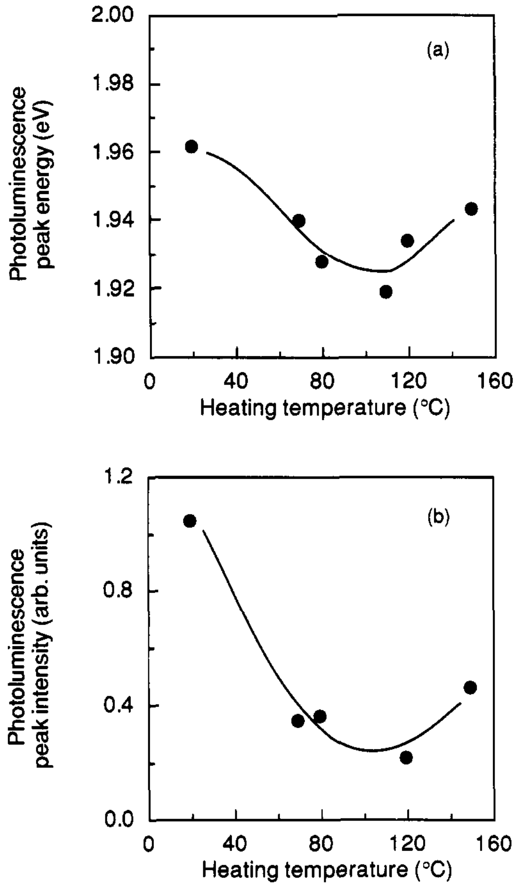

Figure 8. Plots of the peak intensity and the peak energy of photoluminescence against the temperature of the heat treatment.

chain shifts to longer wavelength and its intensity decreases. The dependences of peak energy and luminescence intensity on the temperature of the heat treatment are more clearly indicated in Figure 8. That is, with increasing heating temperature, the emission intensity and the peak energy of luminescence decrease and then slightly increase at higher heating temperature beyond 120 °C. These dependences of the bandgap energy and photoluminescence spectra on heating temperatures can be explained in terms of conformational changes of the polymer main chain after the heat treatment and their influence on the dynamics of photoexcited species as follows.

The photoluminescence intensity of P3AT has been reported to decrease with increase in the effective conjugation length because of increase in the escape probability of the excited species on the main chain from the excited region and decrease in the probability of the radiative recombination of the excited species.[22] That is, these data on the bandgap energy and the photoluminescence intensity indicate an increase in the effective conjugation length and mean coplanarity of the main chain after the heat treatment which also enhanced the crystallinity. The decreased lattice parameter *a*, i.e., the decreased distance between neighboring main chains along side alkyl groups by the heat treatment, possibly enhances the hopping probability of the excited species between main chains and their escape probability from the excited region, which might also result in the decreased probability of the radiative recombination of the excited species.[22,23]

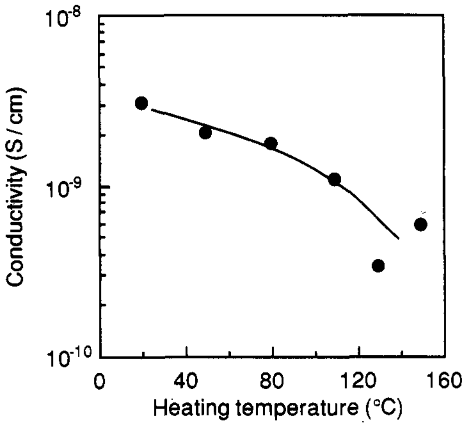

Figure 9. Change in conductivity of P3DT after the heat treatment.

The electronic properties of P3ATs are also expected to show remarkable change through heat treatment. For example, the electrical conductivity of P3AT is expected to increase accompanied with increased crystallinity and coplanarity of main chains after heat treatment. The increase of coplanarity of thiophene rings on a main chain brings the enhancement of effective conjugation length and of intrachain carrier mobility. The decrease of the lattice parameter *a* causes the increase of probability of interchain transfer of the charge carriers in the direction of the *a* axis. Thus, the mobility of charge carrier and the conductivity are expected to increase after the heat treatment.

Figure 9 shows the experimental results on the electrical conductivity after the heat treatment at various temperatures. As is evident from this figure, the conductivity decreased by about 1 order of magnitude with an increase in heating temperature. This anomalous result conflicts with the effect mentioned above. Hence, there should be something that affects the electrical conductivity except for the mobility on the direction of the *c* axis (parallel with the main chain) and of the *a* axis (parallel with the side chain). There might be two possible explanations for this anomaly as follows:

(i) The density of charge carriers induced by the structural defects and by the oxygen or moisture decreased upon heat treatment.

(ii) The probability of charge transfer between neighboring π-conjugation planes along the *b* axis is enhanced upon the heat treatment.

To investigate the first possibility, the ESR measurements were carried out. Before and after the heat treatment, no marked difference in the spin density was observed. Therefore, the changes in the density of polarons on the main chain and, thus, of the density of charge carrier seems to be negligible upon the heat treatment, and the first explanation might be unsuitable.

The lattice parameter *b* was measured before and after the heat treatment to confirm the second explanation by X-ray diffraction measurement as already reported.[24] Figure 10 shows change in the lattice parameter *b* upon heat treatment. The lattice parameter *b* corresponds to twice the distance between neighboring conjugation planes

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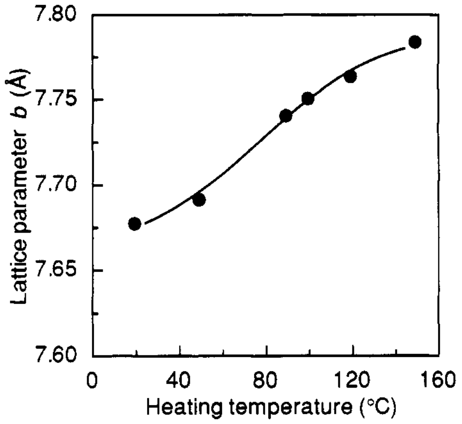

Figure 10. Plots of the lattice parameter *b* against the temperature of the heat treatment.

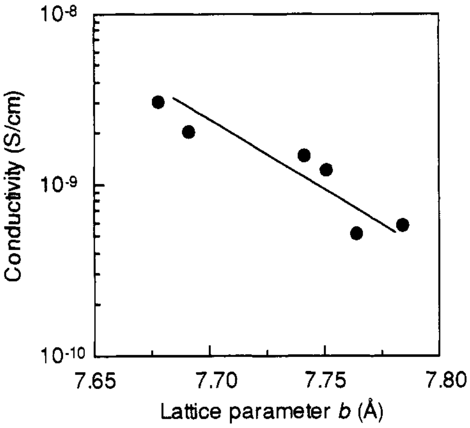

Figure 11. Plots of the conductivity against the lattice parameter *b*.

as shown in Figure 2, though some previous papers have reported a lattice parameter of about half of the present values.[9,25] With an increase in the heating temperature, the lattice parameter *b* was found to increase. This phenomenon is also anomalous since the lattice parameter *a* decreased upon heat treatment and the lattice parameters decrease commonly upon the cooling process after the heat treatment. By this increase in the lattice parameter *b*, however, the anomalous change in the conductivity shown in Figure 9 seems to be explained. That is, with increasing the lattice parameter *b* the carrier migration between neighboring π-conjugation planes along the *b* axis is suppressed, resulting in the smaller carrier mobility and conductivity. Clear exponential change in the conductivity against the lattice parameter *b* was observed as shown in Figure 11 after the heat treatment at various temperature.

Wegner et al. have reported that the conductivity of substituted polypyrroles depends on the distance between main chains and have proposed eq 4 for dependence of

$$W \approx \exp(-2\alpha R)\exp(-E_A/kT) \qquad (4)$$

probability of the interchain carrier hopping (W) on the distance, which is proportional to conductivity.[26] In eq 4 α, R, and E_A are inverse localization length, distance between main chains of closest contact, and energy barrier between the two sites (main chains), respectively. The logarithmic dependence of conductivity on the lattice parameter *b* shown in Figure 11 suggests that the conductivity of this sample is determined by the probability of carrier hopping between the main chains perpendicularly to the conjugation plan on the main chain. Assuming that the lattice parameter *b* is twice of the distance between main chains in closest contact (R) in eq 4, the α value can be evaluated from the results of Figure 11 to be about 160 nm^{-1}, which is much larger than that in the case of polypyrrole derivatives of Wegner's study (2.7 nm^{-1}). Though the origin of this marked difference in the α value is not clear at this stage, some possibilities should be taken into consideration. The first possibility is a difference in samples between the present and the previous works. Wegner et al. have studied electrochemically prepared polypyrrole derivatives in the doped state, while we studied here a chemically prepared undoped sample. Electrochemical doping may affect the α value. The next possible explanation is that the R values in the Wegner's study were estimated by constructing molecular modeling and correspond to the maximum width of the side insulating groups, though in the present work half of the lattice parameter *b* is the closest interplane distance estimated by X-ray analysis. Wegner evaluated R values which are larger than the true interchain distance of closest contact. The third possibility is that half of the lattice parameter *b* in this study might be a good parameter to evaluate the R value in the crystal region but may be not good for the R value in the whole region in the sample film. The mean R value in the whole film should be larger than the half of lattice parameter *b*, since the sample film has a crystallinity as low as 30% and the distance between main chains of closest contact in the amorphous region shold be larger than that in the crystal region. However, the lattice parameter *b* is thought to correlate with the distance between conjugation planes in the amorphous region, since both of them should depend strongly on the conformation of the side alkyl chain as mentioned below.

The related phenomenon has been observed in the case of doped P3AT.[27] In that case, the lattice parameter *b* decreases with increasing the concentration of dopant ions. Not only the carrier density but also carrier mobility has been found to increase upon doping.[28] This phenomenon is also interpreted as the change in probability of the carrier transfer between neighboring π-conjugation planes along the *b* axis. The present results on dependence of conductivity on the higher order structure in P3AT might suggest that the conductivity and carrier mobility of P3AT are determined dominantly with interchain hopping between neighboring main chains stacking in perpendicular to the conjugation plane.

The anomalous increase in the lattice parameter *b* of P3DT after the heat treatment also possibly affects the optical properties. As mentioned above, the intensity of the luminescence decreases with the increase of the crystallinity. However, if we compared the samples with the same crystallinity but treated at different temperatures (e.g., about 70 and 150 °C in Figures 4b and 8b), the larger the lattice parameter *b* becomes, the stronger the luminescence becomes. Judging from the similar bandgap

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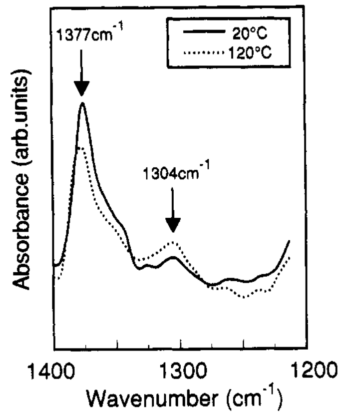

Figure 12. FT-IR spectra of P3DT after the treatments with temperatures of 20 and 120 °C.

energy and the slightly larger lattice parameter *a* in the case of 70 °C (see Figures 5, 6, and 8b), the mobility and escape probability of the photoexcited species in the directions along the main and side chains seem to be the same or larger in the case of 150 °C in comparison with that of 70 °C, which is expected to result in a larger probability of radiative recombinations and, thus, in larger photoluminescence in the latter case. Therefore, the opposite experimental results shown in Figure 8b indicate that the reasons for these spectral changes in photoluminescence can be explained qualitatively in terms of the change of lattice parameter *b*. That is, with larger distances of π-conjugation planes, it is more difficult for the photoexcited species to escape from the excited region perpendicular to the conjugation planes and they are confined more strongly on the main chain, which might result in the enhancement of probability of the radiative recombination and stronger luminescence.

The change in lattice parameter *b* upon heat treatment possibly induced from the conformational isomerization of alkyl chain, since the lattice parameter *b* has been found to increase with increasing the content of gauche form in the alkyl chain depending on the alkyl chain length.[24] The content of gauche form in alkyl chain is, thus, expected to increase upon heat treatment. To clarify this, the FT-IR measurements were carried out.

Figure 12 shows the FT-IR spectra of neutral P3DT films measured at room temperature after treatments with temperatures of 20 and 120 °C. The IR absorption peaks at 1377 and 1304 cm^{-1} have been known to correspond to vibration of the CH_2 moiety of the trans and gauche forms, respectively.[15] The relative intensities of absorption peak at 1304 cm^{-1} against that at 1377 cm^{-1} of the samples treated at room temperature and at 120 °C were evaluated to be 0.27 and 0.38, respectively. The larger relative intensity of the absorption peak at 1304 cm^{-1} in P3DT heated at 120 °C indicates a larger content of gauche conformation than that when evacuated at room temperature (20 °C). The coillike shape of the gauche form alkyl group with the larger diameter and the shorter length in comparison with the case of all-trans form should result in decrease in the lattice parameter *a* and increase in the lattice parameter *b* after the heat treatment as shown in Figure 10. The effects of existence of the bulky gauche conformation that cause the larger lattice parameter *b* and shorter lattice parameter *a* are also reported in the cases of P3ATs with various alkyl chain lengths.[24]

The result of the conformational change in alkyl group after the heat treatment is appeared to be inconsistent with the decreased or constant bandgap energy of the main chain by annealing as mentioned above. The bandgap energy has been reported to increase with increasing gauche form.[8,15] Though the origin of this inconsistency is not clear, we can explain this tentatively as follows. The absorption edge does not change so critically with change in the effective conjugation length longer than 10, since π–π^* absorption peaks of origothiophenes have been known to show no marked dependence on the number of thiophene rings larger than 6.[29] Furthermore, the absorption edge is determined dominantly by the longest effective conjugation length which has substantial distribution. Therefore, the bandgap energy evaluated from the absorption edge should not change drastically upon increase of small amount of gauche form in the side chain.

The content of the gauche form has been reported to increase with measuring temperature.[15] However, the remarkable increase in the content of gauche form observed after the heat treatment is not a phenomenon in the steady state but a kind of phenomena appearing in thermal hysteresis. That is, the gauche form induced in the side chain at the treatment temperature seems to relax incompletely in the cooling process,[10] resulting in the remarkable changes in the crystal structure and the physical properties after the heat treatments. Since the glass transition temperature of P3DT is lower than room temperature,[8] the structural relaxation may occur at room temperature. However, it will still be very slow to relax to a completely stable form at the temperature. The electrical conductivity of P3AT has been known to show a remarkable thermal hysteresis upon a heating–cooling cycle and also slow relaxation within several days.[17] These slow relaxation phenomena should be discussed on the basis of the structural relaxation after the heat treatment. Indeed, we found slow relaxation phenomena after the heat treatment in the electrical properties, in the crystal structure, and in the content of the gauche form in the side chain.[30] Since the measurements in this study were performed in a period of several hours after the heat treatment, any effect of the slower relaxation should be negligible. Detailed results on the relaxation behavior of the physical and structural properties of P3AT should appear elsewhere, as well as a clear dependence of lattice parameters *a* and *b* on the content of gauche conformation in the side chain.[30]

Conclusions

The results in the present experimental study can be summarized as follows:

The crystallinity and the size of the crystallite of P3DT increased upon heat treatment, while the lattice parameter *a* decreased with an increment of the heating temperature.

With increasing crystallintiy by heat treatment, the bandgap energy and the intensity of photoluminescence decreased. These changes can be explained in terms of effectively longer conjugation length in the main chain and the decreased radiative recombination probability of the photoexcited species.

The electrical conductivity decreased with increasing temperature of annealing, while the lattice parameter *b* increased with increment of the heating temperature. The

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interchain transfer of the charge carrier in the direction perpendicular to the conjugation plane is found to affect the electrical conductivity.

After the heat treatment, slight increase in the content of gauche form in the alkyl chain was observed in FT-IR measurement. The existence of the gauche conformation in the alkyl chain is concluded to result in the change in the lattice parameter *b*, after the heat treatment.

Since crystallinity of the present sample is as low as 30%, the lattice parameters of the crystal region may not be good parameters to discuss a overall higher order structure of P3DT. However, the results of FT-IR measurements indicate that the steric hindrance and the mean distance between neighboring conjugation planes should increase in the whole region after the heat treatment. The increase in the gauche conformation in the alkyl groups observed after the heat treatment also suggests a decrease in the distance and a slight increase in the probability of carrier transfer between main chains in the direction of the alkyl groups in the overall region. Note that the most of C–C bonds in the alkyl groups are in the trans conformation even in the amorphous region. Therefore, the mean distance between conjugation planes can be evaluated to increase after the heat treatment along with the lattice parameter *b*, resulting in the decrease in conductivity.