

Molecular Dynamics of Regioregular Poly(3-hexylthiophene) Investigated by NMR Relaxation and an Interpretation of Temperature Dependent Optical Absorption

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Received: July 21, 2009; Revised Manuscript Received: December 15, 2009

The molecular structure and dynamics of regioregulated poly(3-hexylthiophene) (P3HT) were investigated using high-resolution solid-state ^{13}C nuclear magnetic resonance (NMR) and optical absorption spectroscopies. A crystal (C)–plastic crystal (PC) transition induced by the molecular motion of the aliphatic side group was observed for P3HT in the temperature dependence analysis of ^{13}C NMR spectra and spin–lattice relaxation time ($T_{1\rho}$). The aliphatic side group motion in the crystalline state weakened intermolecular π – π interaction, resulting in the blue shift of the characteristic absorption of the interchain exciton. Above the transition temperature, the thiophene twisting motion induces not only further collapsing of the intermolecular interaction but also localizing of the intrachain exciton, leading to the blue shift of the absorption of both the inter- and intrachain exciton.

1. Introduction

Poly(3-alkylthiophenes) (P3ATs), which are a class of representative conjugated polymers, have received significant attention for use in electronic and optoelectronic devices such as a field effect transistor¹ and a photovoltaic cell.² In particular, regioregular 2–5′ head-to-tail coupled poly(3-hexylthiophene) (P3HT) has been widely studied because it provides excellent electrical properties with great solubility and processability due to the hexyl substituents.

The molecular organization for conducting polymers in the condensed state has a marked influence on their optoelectronic or electrical properties.^{3–9} For instance, thermally induced disorder in the alkyl side groups of conjugated oligomers or polymers correlates with the optical absorption.¹⁰ Therefore, understanding of polymorphism which is often observed in comblike conducting polymers is required. For P3ATs, polymorphisms have been found especially in those with longer side groups such as poly(3-octylthiophene) and poly(3-dodecylthiophene), caused mainly from the strong packing tendency of the long alkyl side group and its melting behavior associated with heating.^{11–13} On the other hand, as far as we know, the melting behavior of the hexyl side group in P3HT and related polymorphism have not been reported.

Not only the static structure of P3ATs but also its dynamic structure is crucial to determining its conjugation length, as observed in thermochromism phenomena,¹⁴ in which thermally activated thiophene twisting forms the quasi-ordered structure¹⁵ which behaves as an interrupter of π -conjugation.¹⁶ In spite of its importance, however, only a few studies are available that describe the molecular dynamics of P3HT. High-resolution solid-state NMR techniques offer a promising method to analyze the structure and dynamics of polymers over a wide time range.

Our previous NMR study for poly(3-butylthiophene) (P3BT) has proved the existence of a *twist glass transition*, which is not a conventional glass transition but a glass transition of a thiophene ring twist in the crystalline state at around 340 K.¹⁷ At temperatures greater than the twist glass transition temperature (T_{gp}), most of the P3BT sample takes the plastic crystal (PC) state, in which the polymer undergoes the twist motion of thiophene in the crystalline state. This transition has a considerable effect on IR absorption energy. In the PC state, absorption of the C_β –H out-of-plane vibration band in the IR spectrum appears at 820 cm^{-1} . Below T_{gp} , this absorption shifts to two bands at 825 and 810 cm^{-1} for P3BT. The 825 and 810 cm^{-1} bands originate from the glassy crystal (GC) and the normal crystal (C), respectively. Here, GC contains thiophene rings that are frozen with randomized twisting angles, whereas C contains those without twisting. These phases are clearly distinguished from the amorphous state because IR absorption of C_β –H out-of-plane for amorphous is observed at a higher wavenumber, 832 cm^{-1} . Since the averaged molecular structure in the PC phase is almost the same as the C and GC phases, the phenomenon should be distinguished from the well-known polymorphism found in P3AT.

We tried to analyze the IR spectra of P3HT and obtained a basically similar temperature dependence to P3BT¹⁸ but interpreted them with a different picture for P3HT from P3BT. Below 300 K, two peaks, 826 and 816 cm^{-1} , which respectively correspond to GC and C, grew with cooling, while the 820 cm^{-1} band (i.e., PC) was dominant above 300 K. Therefore, one could regard the transition temperature as T_{gp} for P3HT. However, there was a large difference between P3BT and P3HT, although these polymers showed a similar tendency of IR absorption. A remarkable twist glass transition was not observed by DSC in the P3HT, while the endothermic peak, which is derived from enthalpy relaxation of the thiophene ring twist, was apparent in P3BT. It is considered that the amount of P3HT in the GC state below T_{gp} is smaller than that of P3BT, which is supported by the FTIR results. The main path of PC for P3HT with cooling

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was to the C state, whereas for P3BT it was to the GC state. It should be appropriate, therefore, for introduction of a PC–C transition temperature (T_{cp}) for P3HT instead of T_{gp} . The transition from the PC to C state for P3HT occurred gradually below 300 K because the 820 cm^{-1} band showed gradual change to the 810 cm^{-1} band. In other words, the PC can exist as a supercooling liquid even far below T_{cp} . Why does the difference between P3BT and P3HT occur? One of the most plausible reasons is the difference in behaviors of the side group. So far, the details of side group motion in the crystalline state for P3HT have never been investigated however.

As mentioned above, the dynamic structure is closely connected to the optoelectronic or electronic properties. Tretiak et al. have theoretically found that the vibrational slow torsion and fast bond-stretch motion of π -conjugated molecules are strongly coupled to the electronic structure, and therefore related to the photophysical process.¹⁹ Thus, the details of the dynamic structure for P3HT and of the relationship between its structure and physical properties such as optical absorption are one of the most important issues.

In this study, we present dynamic structures of P3HT in the crystalline state, especially as it pertains to the alkyl side groups, with solid-state NMR results, including temperature dependence of its line shape and spin–lattice relaxation time, T_{1C} . In addition, we shall also report the relationship between the dynamic structure of P3HT and its optical absorption, and discuss a temperature dependence of the conjugation length and its dimensionality.

2. Experimental Methods

Regioregular poly(3-hexylthiophene) (P3HT), $M_n = 45\,000$ and $M_w = 76\,000$, and poly(3-butylthiophene) (P3BT), $M_n = 31\,000$ and $M_w = 45\,000$, were purchased from Rieke Metals Inc. and were used without further purification. The molecular weights were determined using gel permeation chromatography with chloroform as the solvent (calibration with monodispersed polystyrene standards). Here, we should note that GPC measurements on thiophenes against polystyrene standards might cause significant deviations from the true molecular weight. We carried out variable temperature ^{13}C cross-polarization and magic-angle spinning (CPMAS),²⁰ T_{1C} measurements using a NMR spectrometer (JNM-ECA-500; JEOL), equipped with a 4 mm MAS probehead, operating at 500 MHz for ^1H and 125.8 MHz for ^{13}C . For CPMAS and relaxation measurements, experimental conditions were set up with a 90° pulse length of $3.1\text{ }\mu\text{s}$, a contact time of 2 ms, a recycle delay of 3 s, and a MAS rate of 5 kHz. The ^{13}C chemical shifts were referenced externally to the methyl carbon resonance of hexamethylbenzene at 17.4 ppm. We used the Torchia method²¹ for the T_{1C} measurements. The powder samples were used as received.

The FT-IR measurements were carried out using an FT-IR microscope (AIM-8800; Shimadzu Corp.) equipped with an FT-IR hot stage (LK-600; Linkam Scientific Instruments, Ltd.) and a cooling unit (L600A). Samples that had been cast on BaF_2 substrates from the chloroform solution and dried in a vacuum oven for 12 h were cooled at a rate of 10 K/min using nitrogen purging. All IR spectra were recorded at a resolution of 2 cm^{-1} and with an averaging of 16 scans.

UV–vis spectra were measured using a spectrophotometer (V-550, JASCO) equipped with a cryostat (USP203, UNISOKU). All of the samples were cast on a quartz substrate from the chloroform solution and dried in a vacuum oven for 12 h.

3. Results and Discussion

3.1. Temperature Dependence of CPMAS Spectra and FTIR Spectra. To investigate the structure and molecular dynamics of P3HT around the transition temperature (T_{cp}) observed in the previous FTIR study,¹⁸ first we performed ^{13}C CPMAS measurements for P3HT at various temperatures, and the spectra are shown in Figure 1. Four aromatic peaks in the range 120–140 ppm correspond to the four carbons of a thiophene unit and the peaks at higher field than 40 ppm correspond to the aliphatic carbon atoms of the side group. The assignments of each carbon were made comparing the solution NMR studies of P3HT.²² A noteworthy feature is narrowing of spectra with increasing temperature for both main chain and side group. The line shape of NMR reflects the frequency and the amplitude of molecular dynamics. The narrowing probably indicates the onset or acceleration of molecular motion of the P3HT main chain and side group. Parts a and b of Figure 2 show the change in the full width at half-maximum (fwhm) of each peak for the side group and the main chain, respectively.

For the side group, below 370 K, the fwhm decreased gradually with heating, and the slope turned particularly steeper between 200 and 250 K. After that, they showed a weak temperature dependence (note the plateau) between 270 and 300 K, and finally decreased again above 300 K. Interestingly, this transition temperature region for the steeper slope between 190 and 250 K corresponds to that of the previous FTIR study,¹⁸ where the $\text{C}_\beta\text{--H}$ out-of-plane vibration band gradually shifted with heating from two peaks, 826 and 816 cm^{-1} , to the single peak, 820 cm^{-1} , which corresponds to the transition from the GC and C states to PC. In the previous FTIR study, we focused only on the behavior of the thiophene ring moiety, that is, the change in absorption of the $\text{C}_\beta\text{--H}$ out-of-plane region around the transition temperature.¹⁸ The CPMAS spectra, however, imply that the conformation or the mobility of the side group changes around the transition temperature.

In situ FTIR measurements were conducted on thin films of P3HT to elucidate the conformation of the side group. Figure 3 shows the IR spectra in the region of the alkyl C–H stretching between 173 and 293 K, the temperature range that encompasses the transition observed in the NMR measurements. This frequency region around 2920 cm^{-1} (CH_2 asymmetric band) is known to reflect the transition from a “trans” to a “gauche” conformation.^{9,10,23} Nevertheless, there was no noticeable peak shift between trans to gauche in the CH_2 asymmetric band in the measured temperature range. The peak top of the bands was apparent at 2925 cm^{-1} which represents the gauche conformation, while the trans conformation normally exhibits a band at around 2918 cm^{-1} .^{10,23} Thus, the FTIR data shows that the alkyl side group keeps the gauche conformation even below T_{cp} , although the line width of the CPMAS spectra changed in this temperature region.

The ^{13}C chemical shift of CPMAS spectra for the alkyl group is consistent with the IR results. The methylene peaks (C1'--3') at 30.5 ppm maintain the position of the peak top even below T_{cp} . In the case of poly(*p*-biphenylene terephthalate) with *n*-dodecyl side group, whose structure is similar to that of P3AT, that is, consisting of aromatic main chain and alkyl side group, the internal side group signal in the CPMAS spectrum appeared at 30 or 33 ppm.²⁴ When the alkyl side groups crystallized in the all trans zigzag conformation (the immobile region), the signal appeared approximately at 33 ppm, whereas those with rapid exchange between trans and gauche conformations (the mobile region) appeared at about 30 ppm. In our case, the chemical shift of the methylene peak is close to the latter case,

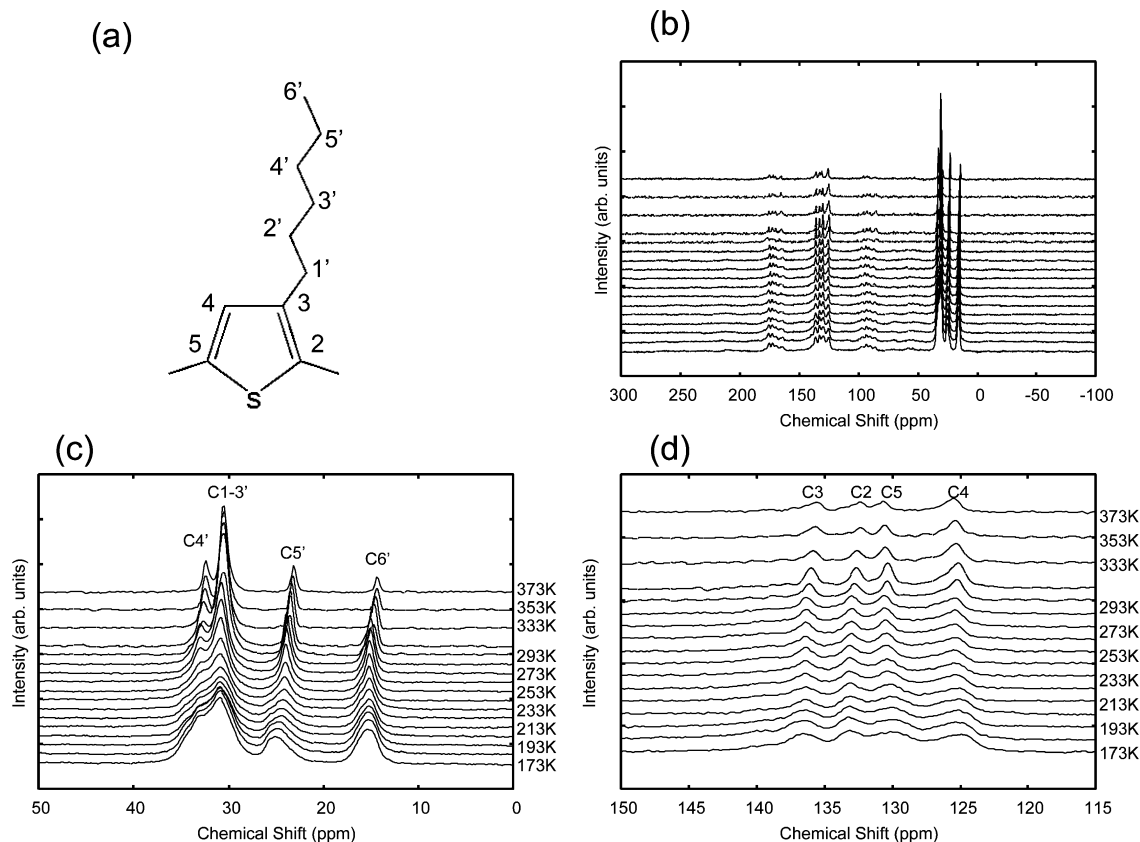


Figure 1. Temperature variation of ^{13}C CPMAS NMR spectra for P3HT. The chemical structure (a), the whole range of spectra (b), the extended spectra for the alkyl carbons (c), and the thiophene ring (d) are shown.

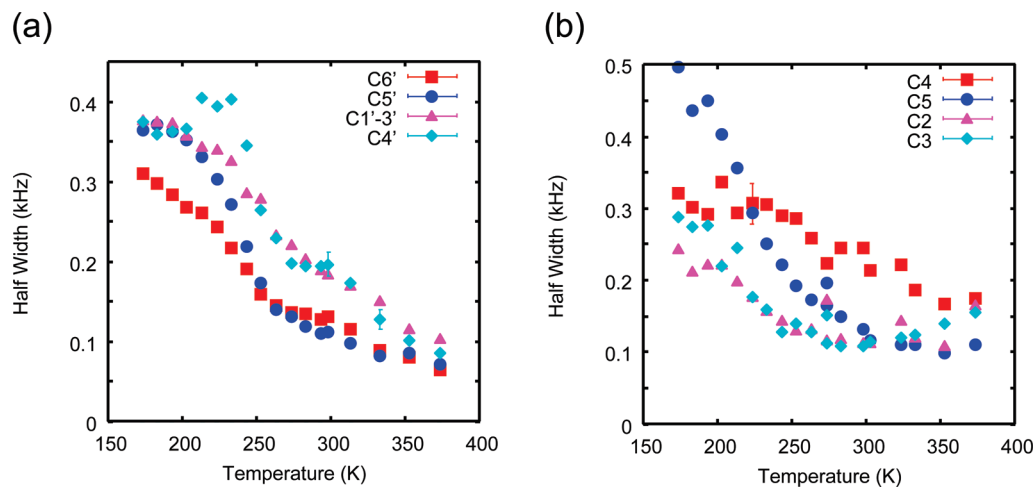


Figure 2. Temperature variation of full width at half-maximum of each ^{13}C CPMAS NMR spectrum for the alkyl carbons (a) and the thiophene ring (b).

suggesting that the side group mainly takes the gauche conformation even below T_{cp} . In fact, CPMAS spectra below T_{cp} showed small shoulders around 25 and 34 ppm in the $\text{C5}'$ and $\text{C1}'\text{--}3'$ signals, respectively, meaning that at least two or more chemically inequivalent methylene carbons in the side group exist below T_{cp} . Our previous FTIR study showed that several phases, PC, GC, C, and amorphous, coexist in this temperature region. These various phases may affect the chemical shift of the side group. In addition, there is a possibility that a small amount of all trans conformation exists because a small shoulder appeared in IR absorption which probably originates from the all trans. Therefore, CPMAS spectra below T_{cp} should be a complicated shape. Unfortunately, the signal of $\text{C4}'$ carbon which appears around 33 ppm overlaps with the

signal of all trans for other methylene carbons. This makes it difficult to assign the conformation at the lower temperature accurately. However, the fact that the signal at 30 ppm is clearly apparent and still being a main component even down to 173 K means that at least a certain amount of the gauche conformation exists below T_{cp} . It has often been claimed that the side groups of P3ATs take a perfect all trans conformation at lower temperatures. However, it is not true for the case of P3HT. Consequently, one can say that the increase of fwhm below T_{cp} originates from the slowing of the side group. At the transition temperature, the side group froze without a conformational change similar to a glass transition. As mentioned above, P3ATs with longer alkyl side group, such as P3OT, P3DT, and P3DDT, show a melting behavior of the side group, and it leads to the

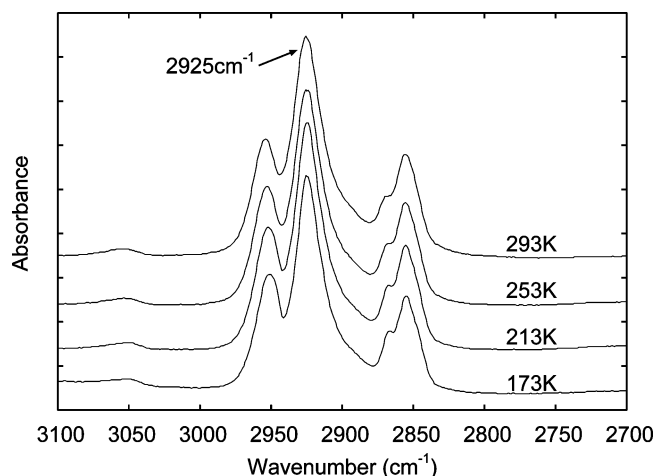


Figure 3. Temperature dependence of infrared absorption spectra in the C–H stretching region of the alkyl side group for a drop-cast P3HT thin film. The samples were cooled at a rate of 10 K·min^{−1}.

polymorphism.^{11,12} On the other hand, the side group transition in P3HT is not an order–disorder transition but a glass transition because of its short side group. Pankaj et al. investigated side-chain dynamics in a series of regiorandom P3ATs by dynamic mechanical analysis, and the α process of the alkyl side group for P3HT was observed at 186 K.²⁵ The fact that the temperature at which the narrowing of the CPMAS spectrum started is almost consistent with their results confirms the glass transition of the alkyl side group in the crystalline state.

Similar to the behavior of the side group, the line width for the main chain also narrowed with heating (see Figure 1d and 2b). Below 300 K, the similar temperature dependence of fwhm to the side group was observed, although slope changes around 190–210 K are not so clear as observed in the side group. The narrowing with heating below 300 K should be attributed to an inhomogeneity–homogeneity change in the conformation or to acceleration of the thiophene ring twisting motion, or acceleration of the thiophene ring twisting motion. Indeed, the IR band of the C β –H out-of-plane vibration below 300 K, T_{cp} , was able to be decomposed to four components, PC, C, GC, and amorphous, while decomposed to two states, PC and amorphous, above T_{cp} .¹⁸ Therefore, both disappearance of conformational distribution and increase of mobility must have contributed to the narrowing of CPMAS signals.

3.2. $T_{1\rho}$ Measurements. Next, we performed ¹³C spin–lattice relaxation-time measurements using the conventional Torchia method at various temperatures to investigate the molecular dynamics around the transition observed in the FTIR and CPMAS NMR measurements. The relaxation rates ($R_{1\rho} = T_{1\rho}^{-1}$) for each carbon at various temperatures are plotted in Figure 4.

For the side groups (Figure 4a), each R_1 value was obtained using a stretched exponential fitting curve

$$M_z(t) = M_z(0) \exp(-R_1 t)^\beta \quad (1)$$

where M_z is the magnetization along the magnetic field and β is the stretching parameter. Whereas below 230 K the relaxation rates were distributed, above 250 K, the value of β showed nearly unity (see the relaxation curves in the inset of Figure 4a); that is, the obtained fitting curve was simple exponential. It suggests that a transition from several phases to a single phase with heating occurred. The temperature range where the β value is turned into unity corresponds to the CPMAS spectrum

narrowed, suggesting the side group transition. However, a clear transition of R_1 was not observed at the range probably due to volatility of R_1 , which is very susceptible to plots with low amplitude in the relaxation curve. With further heating, $R_{1\rho}$ reached the maximum value around 270–300 K, except for the methyl carbon of the side group, which decreased with heating, meaning that the correlation time, τ_c , for the inner side group reached the inverse of larmor frequency, 125 MHz. At a temperature greater than 300 K, the molecular motion of these carbons entered the extremely narrowing regime,²⁶ and eventually $R_{1\rho}$'s decreased with heating. Interestingly, the onset temperature of extremely narrowing regime is consistent with T_{cp} , indicating that rapid alkyl group motion occurs in the PC state.

As mentioned above, the decay of magnetization of the side group carbon obeyed Debye type relaxation in this temperature range. In this case, we can determine the activation energy of correlation from temperature dependent R_1 as follows. The spectral density function $J(\omega)$ is described as

$$J(\omega) = \frac{\tau}{1 + \omega^2 \tau^2} \quad (2)$$

and especially in the extremely narrowing regime, that is, $\omega\tau \ll 1$, eq 2 is given by

$$J(\omega) \approx \tau \quad (3)$$

The relation between R_1 and $J(\omega)$ is given via the second moment M_2 of fluctuating local field as

$$R_1 = M_2 J(\omega) \quad (4)$$

and

$$R_1 \approx M_2 \tau \quad (5)$$

when $\omega\tau \ll 1$. Unfortunately, absolute M_2 was not determinable from the CPMAS spectra. However, the fact that line widths of the side group carbons are almost constant in the temperature region, above 270 K, suggests that M_2 's of these carbons would also be almost constant. Eventually, the activation energy of correlation time can be obtained from Figure 4 by using the following equation:

$$R_1 \approx M_2 \exp\left(\frac{E_a}{RT}\right) \quad (6)$$

and the resulting activation energies, E_a , of 8.2–15.0 kJ/mol (Table 1).

For the main chain carbons, the decay of magnetization obeyed the stretched exponential fitting curve, given as $M_z(t) = \exp(-R_1 t)^\beta$, in all measured temperature ranges as shown by the representative curves in Figure 4b. This dispersion of R_1 is reasonable for the following reasons. Below T_{cp} , some chains form GC in which the relaxation rate disperses. In addition, the other phases or states, namely, C, PC, and amorphous, as well as GC, coexist in the temperature range. Even above T_{cp} , at least two phases, PC and amorphous, exist. Moreover, we cannot ignore the fluctuation of intermolecular interaction, because of the packing effect in the crystalline state such as C,

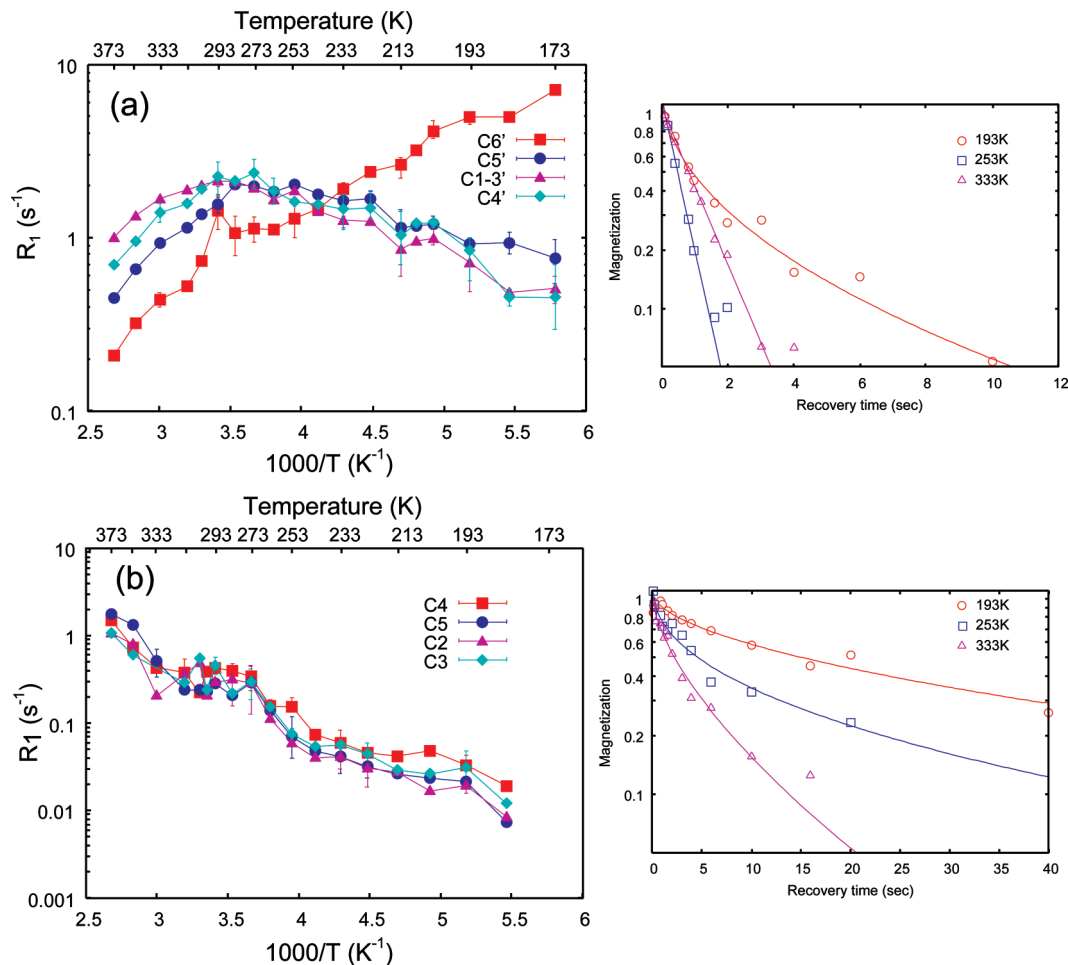


Figure 4. Plots of ^{13}C spin-lattice relaxation rate R_1 for P3HT for the alkyl side group (a) and the main chain (b). Part a is obtained by single exponential fitting using the plots above 0.1 of the normalized magnetization. Typical decay curves are also shown for the hexyl $\text{C5}'$ carbons, and for the thiophene C4 carbon at -193 , 253 , and 333 K (insets).

TABLE 1: Activation Energy, E_a , Estimated from the Temperature Dependence of R_{1C} for (a) the Side Chain and (b) the Main Chain

(a)				
temperature (K)	E_a (kJ/mol)			
	$\text{C6}'$	$\text{C5}'$	$\text{C1}'\text{--}3'$	$\text{C4}'$
$T > 290$	15.0	13.0	8.2	12.0
(b)				
temperature (K)	E_a (kJ/mol)			
	C3	C2	C5	C4
$T < 250$	7.4	7.8	8.2	6.5
$250 < T < 270$	18.0	28.4	18.5	22.2
$T > 310$	24.0	25.5	28.1	29.7

GC, and PC. Therefore, not only the spectral-density functions of intramolecular $J_{\text{intra}}(\omega)$ but also those of intermolecular $J_{\text{inter}}(\omega)$ are needed to determine T_1 . Accordingly, the decay curve cannot be expressed by a single stretched-exponential function at the measured temperatures, resulting in the complicated behavior of the stretching parameter.

Obtained R_1 's are shown in Figure 4b. Two step jumps with heating are visible around 240 and 310 K. The abrupt slope change in the lower temperature region seems to correspond with the fwhm change observed in the alkyl side group. We can describe a plausible scenario of the transition; the alkyl chain

begins to undergo molecular motion around 200 K, which is the onset of slope change in the fwhm, upon heating, and then the thiophene begins to twist around 240 K in response to the side group motion accelerated enough to stimulate the main chain motion. Around 270–310 K, R_1 's show almost constant values. This plateau of R_1 probably is related to the critical behavior of C–PC transition. The details are discussed later in this section. At a temperature greater than 310 K, R_1 increases again with heating. The steep rise of R_1 was observed in the case of the twist glass transition for P3BT as well.¹⁷ We believe that all thiophene rings undergo twisting, which means that they are in the PC state.

The twisting angle of thiophene ring should markedly affect the activation energy of the twisting motion.^{27–29} In other words, if we can calculate the activation energy, we can determine the amplitude of twisting motion. Unfortunately, however, we cannot determine the exact activation energy because of complicated factors as follows. When the relaxation follows the stretched function, the spectral density function should be given not by the Debye function but by complicated functions which contain exponents such as the Cole–Cole, the Cole–Davidson, and the Havriliak–Negami (HN) function.³⁰ Here, we show the HN function as an example

$$J(\omega) = -\frac{1}{\omega} \text{Im} \left[\frac{1}{[1 + (i\omega\tau)^\beta]^\alpha} \right], \quad (0 \leq \alpha, \beta \leq 1) \quad (7)$$

Moreover, two interactions, magnetic dipolar coupling and chemical shift anisotropy, should be considered because they can affect each $J(\omega)$ in the specific ratio depending on the second moment of the interactions. These factors prevent an estimation of exact activation energy for the thiophene twist. Thus, we shall roughly estimate the activation energy only for readers' information by using the Debye function from the stepwise temperature dependence of the R_1 (Table 1). In the slow motion regime, i.e., $\omega\tau \gg 1$, eq 4 is given by

$$R_1 \approx M_2 \frac{1}{\omega^2 \tau} \quad (8)$$

$$\approx \frac{M_2}{\omega^2} \exp\left(-\frac{E}{RT}\right) \quad (9)$$

Below 240 K ($1000/T \sim 4.2$), the activation energy is 6.5–8.2 kJ/mol. Between 240 and 270 K, the slope grew steep, resulting in the increase of the activation energy, 18.0–22.0 kJ/mol. This implies that the twist angle in the temperature range increased due to the alkyl side group motion which is already more accelerated than below 240 K.

Interestingly, R_1 s remain almost constant values around 270–310 K. A similar phenomenon has been reported for the phase transition of the second kind between a high-temperature normal phase and a structurally incommensurately modulated phase, T_i , particularly named “partial slow motion limit” in some insulating crystals.³¹ Just above the critical temperature, R_1 is temperature independent due to the critical slowing down of order parameter dynamics.³¹ The fact that the temperature independent region is observed just above T_{cp} for P3HT might indicate that the transition could be a second-order phase transition as well. The absence of remarkable latent heat in DSC¹⁷ also supports the second-order phase transition. On the contrary, however, the phenomenon that violates the general property of second-order transition has also been observed; that is, PC can exist even below T_{gp} as the supercooling liquid.¹⁸ Further investigations such as the frequency dependence of T_{1c} exchange NMR measurements are necessary to determine the classification of the phase transition occurring in P3HT.

In the temperature range greater than 310 K, namely, the PC state, the activation energy increased further to 24.8–29.7 kJ/mol, which is the maximum in the measured temperature range, suggesting that the twisting angle of the thiophene ring became larger in the PC state than those in GC or C.

The temperature dependent R_1 also provides information about the difference of dominant structures between P3BT and P3HT around T_{gp} or T_{cp} . For the P3BT, only the C4 carbon, which is directly connected to a proton, showed larger R_1 than other carbons below the twist glass transition temperature ($T_{gp} = 340$ K),¹⁷ indicating that the relaxation was caused mainly by ^{13}C – ^1H magnetic dipolar coupling. The thiophene ring would not undergo reorientations sufficient to fluctuate the chemical shift anisotropy (CSA). Above the T_{gp} , on the other hand, the other carbons (C2, C3, C5) showed specific slopes individually, where reorientation of the thiophene ring, i.e., twisting, brought about fluctuations in CSA as well. For P3HT, however, all carbons showed similar R_1 in the measured temperature range, suggesting that the relaxation occurred not only by the fluctuation of magnetic dipolar coupling but also by that of chemical shift anisotropy even below T_{cp} .

This difference between P3BT and P3HT seems to be consistent with our argument based on the previous IR results;

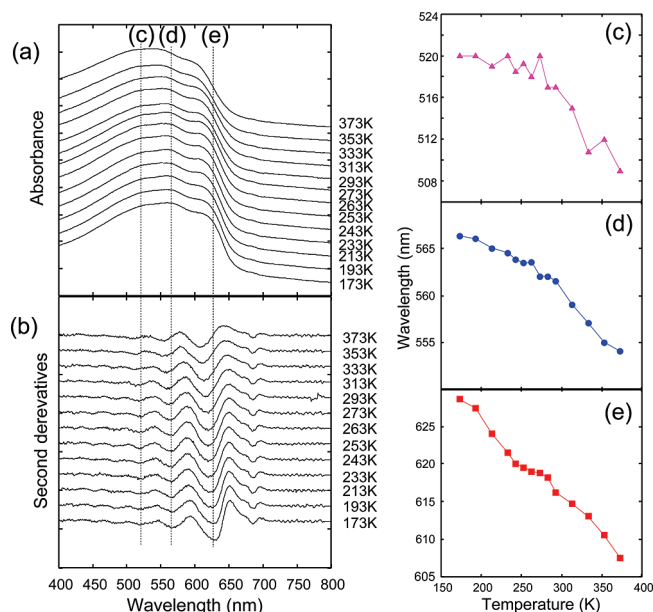


Figure 5. UV–vis spectra of P3HT at the indicated temperatures (a), their second derivatives (b), and plots of the three peak tops of the second derivatives as a function of temperature (c–e).

GC and C, in which thiophene does not undergo twisting motion, are dominant in P3BT, whereas PC is dominant in P3HT below T_{gp} or T_{cp} . This tendency can be explained by the degree of frustration against crystallization due to interchain interaction, as discussed in the previous report.¹⁸ In the case of P3BT, locally favored structures exist with strong frustration. Consequently, GC and C are preferentially realized with respect to a decrease of temperature. For P3HT, in contrast, PC is the dominant structure instead of GC or C because of its weak frustration. The relationship between the molecular mobilities of the side group and main chain supports this hypothesis. The C–PC transition occurred in P3HT when the hexyl group entered the extreme narrowing regime, which is confirmed by a negative slope of R_1 vs T^{-1} . In other words, π – π packing is easily weakened by the rapid side group's motion. On the other hand, P3BT kept GC and C states even though the butyl group was in the extremely narrowing regime. The stronger intermolecular interaction in P3BT yields a more rigid crystal as well as a large amount of GC.

3.3. Variable-Temperature UV–vis Spectra. To investigate the effect of the transition on the conjugation length, variable-temperature UV–vis absorption measurements were performed. Figure 5 shows UV–vis spectra for the P3HT cast film on mica. Resolved features were visible at around 520, 560, and 620 nm.

Brown et al. investigated the effect of interchain interactions on the absorption and emission of P3HT in detail.³² The absorption at 620 nm is a characteristic feature at the onset of the $\pi - \pi^*$ transition due to the interchain interactions. In contrast, the higher energy peaks at 560 and 520 nm are, respectively, origins of 0–0 and 0–1 transition of the intrachain excitons. In the case of amorphous regiorandom (rra) P3HT, the absorption spectrum showed a blue shift with respect to the regioregular (rr) P3HT absorption, and the maximum peak appears around 450 nm without a resolved vibrational peak.^{32–34} This is usually attributed to a decrease in the effective conjugation lengths of the chain segments. In the temperature range we measured, the absorption of the rr-P3HT showed no large blue shift to the peak of amorphous, indicating that interchain packing, namely, the π -stacking, was maintained at least until 373 K.

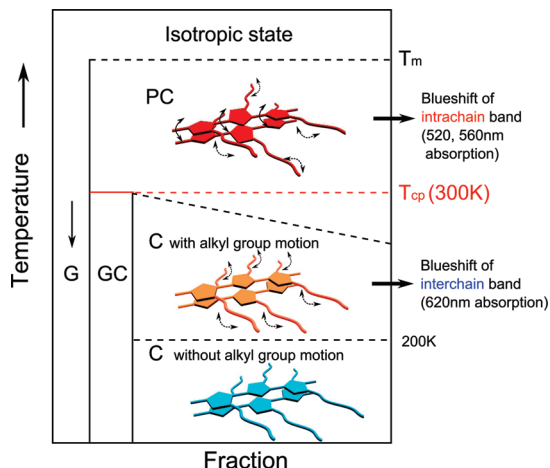


Figure 6. Proposed scheme of the phase transition and the relation to the absorption spectra. The horizontal axis exhibits the fraction of phases estimated by the FTIR measurements in the previous paper.¹⁸

In order to investigate the change in the UV-vis spectra in detail, second derivatives of the spectra are shown in Figure 5b, and the wavelengths at the tops of the three peaks are plotted as a function of temperature in parts c–e. An interesting point about the spectral change is differences in the behaviors of three peaks below and above 270 K, where the onset temperature, T_{cp} , of the thiophene twisting was observed in the FTIR and NMR measurements. Between 170 and 270 K, the peak around 620 nm, which is of intermolecular origin, showed a large blue shift from 629 to 617 nm ($\Delta = 0.040$ eV) with heating compared to the other two features; the 0–0 intramolecular band around 560 nm showed a small shift from 566 to 562 nm ($\Delta = 0.015$ eV) and the 0–1 intramolecular band around 520 nm was temperature independent. In this temperature region, the alkyl groups undergo a glass-transition-like behavior. The blue shift of the lowest energy feature around 620 nm at lower temperature suggests that alkyl chain motion in the crystalline state weakens the intermolecular face-to-face π – π interaction, which would reduce the intermolecular orbital overlap and the strength of the exciton coupling, resulting in the higher π – π^* transition energy. However, because a certain amount of thiophene moieties still maintain planarity, the intrachain features are considered to be less dependent on temperature.

At temperatures greater than 270 K, in contrast, all of these features exhibited blue shifts with 0.03–0.04 eV. Around 270–290 K, all thiophene rings start to twist; namely, they are in the PC state. The corresponding features of the intrachain exciton are greatly dependent on the degree of intrachain order of the polymer chain.³² The twisting motion is crucial to the intrachain order; consequently, not only the peak of the intermolecular origin but also the two peaks of the intrachain origin showed a blue shift in the PC state upon heating. The dimensionality of conjugation shortened step-by-step with each transition of the side group and the main chain. A proposed scheme for the relationship between the molecular dynamics and the absorption is shown in Figure 6.

4. Conclusion

The solid-state structure and dynamics of the regioregulated P3HT around the crystal (C)–plastic crystal (PC) transition, observed in the previous FTIR study, were investigated using ¹³C NMR and optical absorption spectroscopies. When heating P3HT films from low temperature, we observed the following structural transitions. First, the alkyl side group began to move

around 200 K, which is supported by the variable temperature CPMAS measurement. This transition is not a simple order–disorder transition but that without a conformational change; the transition keeps a gauche conformation, similar to the glass transition. It has been often explained that the all trans conformation of the alkyl side group induces the main chain planarity. However, our NMR and IR results showed that a perfect all-trans alignment is not necessary for the crystalline state with thiophene π – π stacking of P3HT.

The C–PC transition occurred around 270–290 K. Above the temperature P3HT took PC state, in which the thiophene ring undergoes twist motion. The side group motion was also accelerated in this temperature region, as characterized by transition from the slow motion regime to the extremely narrowing regime in the temperature dependent T_{1C} measurement. Variable-temperature UV–vis measurements provided the relationship between the dynamic structure and the conjugation length. The lowest energy absorption peak around 620 nm, which is the intermolecular π stacking origin, showed a blue shift in both temperature regions, i.e., below and above T_{cp} . The side group motion probably weakened the interchain interaction, resulting in a blue shift, although the thiophene ring maintain a rigid planar conformation. On the contrary, the intrachain vibrational peaks, 0–0 (560 nm) and 0–1 (520 nm), showed a weak or no shift below T_{cp} . This indicates that the intrachain exciton can extend along the main chain as long as the thiophene rings keep a planar or almost planar conformation even the side groups move rapidly. With thiophene twisting, i.e., in the PC state, these two features show a blue shift. As is well-known, the thermochromism phenomenon becomes prominent in the PC state. The sudden decrease of fwhm for the CPMAS signal for the main chain strongly supports this twisting transition.

Acknowledgment. One (N.A.) of the authors is supported by the Ministry of Education, Culture, Sports, Science and Technology (Japan) through a Grant-in-Aid for science research (No. 20655049).

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JP910590D