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Thermal relaxation in the electrical conductivity and structure of poly(3-dodecylthiophene)

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Abstract. The conductivity of poly(3-dodecylthiophene), which decreases after a heating–cooling cycle, again increases to the original value in a period of several days, while ESR and the optical properties showed no marked relaxation phenomenon. The crystal structure of poly(3-dodecylthiophene) studied by x-ray diffraction measurements also showed marked changes in its lattice parameters a and b in the same period after the heat treatment. Relaxation to the original smaller b-value which corresponds to twice the distance between the neighbouring two conjugation planes was observed after the heat treatment. This is regarded as the origin of the relaxation in the conductivity. Thus, the increase in conductivity during the relaxation is interpreted in terms of the increase in the probability of inter-chain hopping of charge carriers and therefore carrier mobility with decreasing lattice parameter b. Conformational relaxation from *gauche* type to *trans* type was also observed in an FTIR analysis of the side alkyl chains.

1. Introduction

Conducting polymers having processability have attracted much attention not only from the practical viewpoint but also from the fundamental viewpoint [1–5]. Among various processable conducting polymers, poly(3-alkylthiophene) (P3AT), shown in figure 1, is one of the most interesting, since P3AT shows various unique properties such as solvatochromism [6], gel behaviour [7–9], electroluminescent behaviour [10], photoinduced solubilization [11], photocatalytic properties [12] and anomalous temperature dependences in electrical and optical properties such as thermochromism and the related phenomena [13–19].

We have reported various unique thermal properties of P3AT. The band-gap energy of P3AT evaluated from the threshold energy of visible absorption spectra changes drastically at the melting point, while the absorption peak energy changes gradually depending on the temperature in the pre-melting region [13]. The photoluminescence spectrum of P3AT which corresponds to recombination of excitons on the π-conjugation system also shows anomalous enhancement with increasing temperature and a marked blue shift in the pre-melting region [16]. These unique temperature dependences of the optical properties can be explained by the decrease in effective conjugation length caused by conformational changes in the side and main chains [20]. These drastic changes in optical properties depending on temperature have never been observed in other alkyl-substituted five-membered heterocyclic conducting polymers such as poly(3-alkylselenophene) and poly(3-alkylfuran) [21]. The electrical conductivity of P3AT also shows an anomalous temperature dependence [22, 23]. In the pre-melting region, the conductivity of P3AT increases with increasing temperature and, after a maximum, again decreases at higher temperatures. At the melting point, a stepwise decrease in conductivity was observed and then an Arrhenius-type temperature

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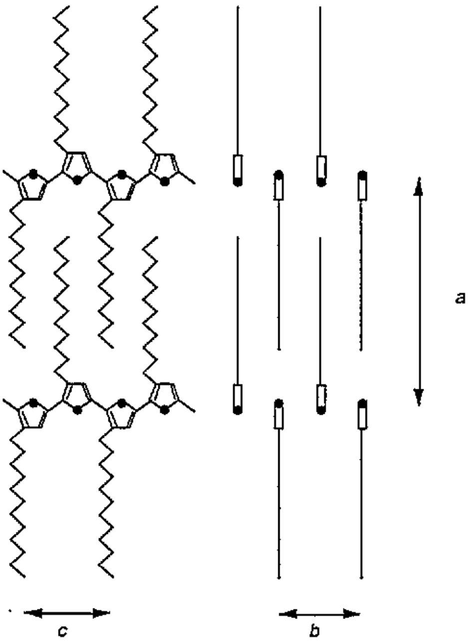

Figure 1. Orthorhombic lattice structure of P3DT.

dependence was observed in the liquid state [22]. Furthermore, after a heating–cooling cycle, a marked decrease in conductivity has been observed in comparison with that before the heat treatment. The decreased conductivity has been found to increase again in a period of several days, converging to the initial value [23].

More recently, we studied the thermal hysteresis in conductivity, optical properties and structure of poly(3-dodecylthiophene) (P3DT) [24]. The lattice parameter *b* in the orthorhombic lattice structure shown in figure 1 [20], corresponding to twice the distance between neighbouring conjugation planes on main chains, was found to increase after the heat treatment. Since clear exponential correlation between decreasing conductivity and increasing lattice parameter *b* has been observed, as in the case of substituted polypyrrole studied by Wegner and Ruhe [25], the change in the lattice parameter *b* was concluded to result in decreased electrical conductivity after the heat treatment. A considerable increase in the *gauche* form conformation of the side alkyl chain was also observed in the Fourier-transformed infrared (FTIR) measurement after the heat treatment. These experimental results indicate that the higher-order structure of P3DT is different from that in the initial state, resulting in marked thermal hysteresis in the electronic properties. Therefore, the thermal relaxation phenomena possibly cause changes in the higher-order structure of P3DT.

In the present paper, the slow relaxation processes in the properties and structure of P3DT after the heat treatment are studied in detail.

2. Experimental details

The P3DT used here was prepared by the chemical polymerization method utilizing $FeCl_3$ as a catalytic oxidizing reagent and purified carefully as already described [3]. The P3DT film was formed on appropriate substrates such as Teflon film, quartz plate and indium-tin-oxide-coated quartz plate from chloroform solution by the casting or the spin-coating methods.

The P3DT film was evacuated for 2 h at room temperature to remove residual solvent and heated for 3 h at various temperatures; then the sample was cooled slowly with a cooling rate of 30 °C h^{-1}. These heat treatment procedures were performed under vacuum.

X-ray diffraction measurements were performed by utilizing the RINT-1100 system (Rigaku) with the Cu Kα line of 1.54 Å wavelength. UV–visible absorption spectra and photoluminescence spectra were measured by utilizing a Hitachi 330 spectrophotometer and a Hitachi F-2000 fluorescence spectrophotometer, respectively. The electrical conductivity was measured by the two-probe method under vacuum. FTIR spectra were measured utilizing a JASCO FT/IR-3 spectrometer. All these measurements were carried out at room temperature (about 20 °C).

3. Results and discussion

The electrical conductivity of P3DT was measured at room temperature after heat treatment at various temperatures. As has been mentioned in the previous paper [23], the room-temperature conductivity decreased after heat treatment at a temperature ranging from 50 to 170 °C. The decreased conductivity was found to increase again slowly, converging to the initial value measured before the heat treatment (just after the evacuation at room temperature) in all cases. For example, the slow relaxation of the conductivity of P3DT is shown in figure 2.

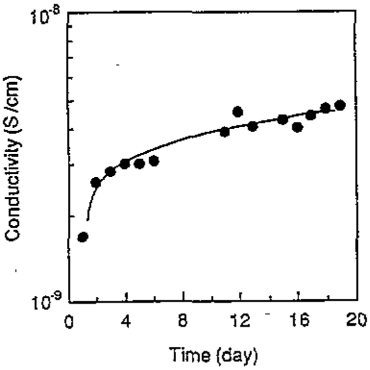

Figure 2. Relaxation of conductivity of P3DT after heat treatment at 170 °C.

Contrary to the anomalous increase in conductivity over several days at room temperature after cooling from the temperature of the heat treatment, the magnetic and optical properties did not show any relaxation phenomena after the heat treatment. No marked change was observed in the ESR spin density for several days after the heat treatment, suggesting negligible change in the number of polarons on the main chains and carrier density. The band-gap energy evaluated from the visible absorption spectra and photoluminescence spectra also showed no marked variation after the heat treatment. These results are interpreted to indicate that the slow relaxation phenomenon in the conductivity is related to neither the change in carrier concentration nor the change in effective conjugation length which affects the carrier mobility along a main chain. That is, if the effective conjugation length increased, red shifts of absorption and photoluminescence peaks should result.

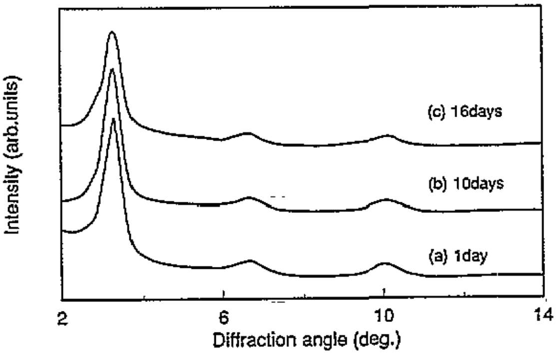

Figure 3. Change in x-ray diffraction spectra at room temperature after heat treatment at 170 °C.

To clarify the origin of the relaxation in conductivity, the higher-order structure of P3DT was studied by x-ray diffraction measurement after the heat treatment. Figure 3 shows the change in the x-ray diffraction spectrum in several days after the heat treatment. The diffraction intensity of a peak at around 3° which corresponds to (100) diffraction increases and the peak angle becomes larger over several days. These x-ray spectra indicate relaxation in the degree of crystallinity and lattice parameters.

The crystallinity of the P3DT film was evaluated using equations (1) and (2) as follows [26,27];

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

$$X_c = \frac{1}{1+KR} \qquad R = \frac{I_a}{I_c} \qquad K = \frac{I_{100c}}{I_{100a}} \tag{2}$$

where I_c and I_a are the integrated intensities of x-rays scattered by the crystalline region and the amorphous region, respectively. A clear linear relationship was observed between I_a and I_c of various samples of different crystallinities, allowing us to estimate I_{100c} and I_{100a} for the P3DT film. The degree X_c of crystallinity is evaluated using equation (2) and summarized in figure 4. Here, the x-ray intensity in the region of the diffraction angle between 2° and 20° was taken into account since x-ray signals out of this angle region were very weak. The error bars given in figure 4 are mainly caused by uncertainty in the integration of the x-ray signal.

The crystallinity of P3DT was found to decrease over several days after the heat treatment. The origin of this relaxation in crystallinity is not clear at this stage, since this increase in the crystallinity seems to be a complicated phenomenon depending on the cooling rate. We speculate here tentatively that the stress and/or the tension induced in the sample film by volume change upon cooling may result in this relaxation in the crystallinity. The slow increase in conductivity shown in figure 2 cannot be explained by this relaxation in

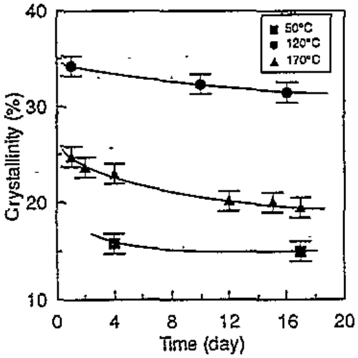

Figure 4. Change in crystallinity at room temperature after heat treatment at various temperatures.

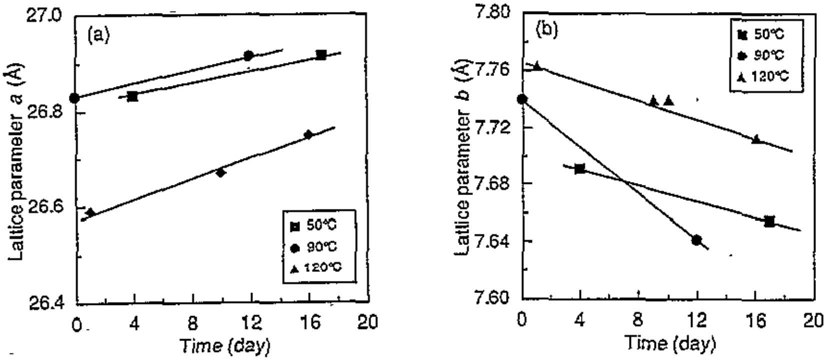

Figure 5. Change in lattice parameters *a* and *b* at room temperature after heat treatment at various temperatures.

crystallinity, since the carrier mobility is thought to increase with increasing crystallinity in polycrystalline samples.

Figure 5 shows the changes in the lattice parameters *a* and *b* after heat treatments at various temperatures. The lattice parameter *a*, which corresponds to the distance between the two neighbouring main chains which have the same conjugation plane, increases with time after the heat treatment, while the lattice parameter *b*, which corresponds to twice the distance between main chains in the direction perpendicular to the conjugation plane, decreases over a period of several days. It should be noted that these lattice parameters *a* and *b* immediately after the heat treatment were smaller and larger, respectively, than those measured before the heat treatment as is also evident in figure 5. That is, these lattice parameters change upon heat treatment and then relax back slowly to the initial values after the heat treatment. The slow decrease in the lattice parameter *b* may be the origin of the slow relaxation in conductivity after heat treatment, since a clear exponential decrease in conductivity against increase in the lattice parameter *b* has been observed for P3DT [24]. The suppression effect on the carrier mobility which is expected to be induced by the increase in the lattice parameter *a* upon thermal relaxation seems to be negligible. That is, the electical conductivity of P3AT strongly depends on the inter-chain carrier transfer between neighbouring main chains in the direction perpendicular to the conjugation plane (parallel to the b axis), but not in the direction parallel to the alkyl side chain (parallel to the a axis). In the latter direction, the distance between neighbouring main chains seems to be too large and the relative change in the lattice parameter a upon thermal relaxation is too small to result in considerable changes in the possibility of inter-chain carrier transfer and in the conductivity. On the other hand, the distance between neighbouring conjugation planes (half the lattice parameter b) of about 3.8 Å, which is close to that in graphite of 3.35 Å [28], is fairly short, and it is reasonable to interpret that the inter-chain hopping of the charge carrier occurs dominantly in this direction. Therefore, a small decrease in the lattice parameter b upon relaxation can result in an increase in conductivity.

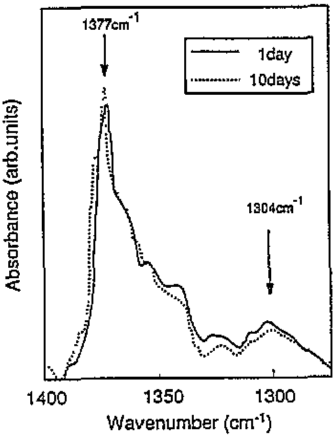

Figure 6. FTIR spectra of P3DT immediately after and 10 d after heat treatment.

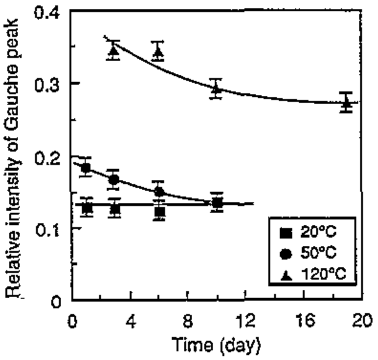

Figure 7. Change in the relative intensity of the absorption peak at 1304 cm^{-1} at room temperature after the heat treatment at various temperatures.

The lattice parameter b of P3AT with different lengths of alkyl side chain has been observed to be affected by conformational isomerization of the alkyl side chain [29]. The effects of conformational change in the alkyl side chain on the structural relaxation were hence studied by measuring FTIR spectra in a wavenumber range corresponding to the CH_2 wagging mode. Figure 6 shows the FTIR absorption spectra of a P3DT film measured immediately and 10 days after the heat treatment. The clear absorption peak at 1377 cm^{-1} can be attributed to the trans–trans CH_2–CH_2 structure, while the small peak at 1304 cm^{-1} is attributable to the CH_2–CH_2 unit in the gauche–gauche conformation [20]. Small side bands between these two peaks can be assigned to combined structures of the *trans* and the *gauche* conformations [20]. As evident in this figure, the intensity of the absorption peak at 1304 cm^{-1} slightly decreased and that at 1377 cm^{-1} slightly increased over the period of 10 days after the heat treatment. The relative intensities of the peak at 1304 cm^{-1} against that at 1377 cm^{-1}, which correspond to the relative amounts of *gauche* conformation, are plotted in figure 7 against time after the heat treatment. As shown in this figure, the relative intensity of 1304 cm^{-1} decreases after heat treatment at 100 and 120 °C while no marked variation was observed in the sample without heat treatment over several days. That is, the amount of *gauche* conformation in the side chain, which increased immediately after the heat treatment, relaxes to the initial state over several days. It should be noted that the amount of *gauche* conformation has been reported to increase in the pre-melting region [20]. Furthermore, a clear correlation was found between the relative intensity of the absorption peak at 1304 cm^{-1} and the lattice parameters a and b as shown in figure 8. That is, when the relative intensity of the 1304 cm^{-1} peak is small, the lattice parameter a is large but b is small. These relationships are reasonable if the relatively short length and the bulky shape of the alkyl chain containing considerable *gauche* conformation in comparison with those of the all-*trans* alkyl chain were taken into account [29]. The widths of the alkyl chain in the all-*trans* and the all-*gauche* forms are evaluated to be about 4 Å and 5.5 Å, respectively, from the molecular modelling. In the latter case, the alkyl chain is thought to have a coil-like shape [29]. The lattice parameter b of about 7.7 Å is roughly twice the width of the alkyl chain in the all-*trans* form (3.7 Å × 2). Thus, the lattice parameter b changes with change in the amount of *gauche* conformation in the side alkyl chain. The linear change in the lattice parameter a shown in figure 8 is also reasonable, since it has been found to increase linearly with increasing alkyl chain length shorter than 12 [29]. It should also be mentioned that the regression line shown in figure 8(b) intersects the lattice parameter b axis at about 7.55 Å, which agrees with the value of lattice parameter b of P3ATs having alkyl chains shorter than 10 which contain only *trans* conformation at room temperature. In contrast, the regression line shown in figure 8(a) intersects the lattice parameter a axis at about 27.4 Å, which also agrees with the value expected on the basis of a linear relationship between the lattice parameter a and the alkyl chain length shorter than 10 for P3DT if it has a side chain of all-*trans* conformation. These agreements confirm the linear relationship between the amount of *gauche* conformation in the side alkyl chain and the lattice parameters, as shown in figure 8.

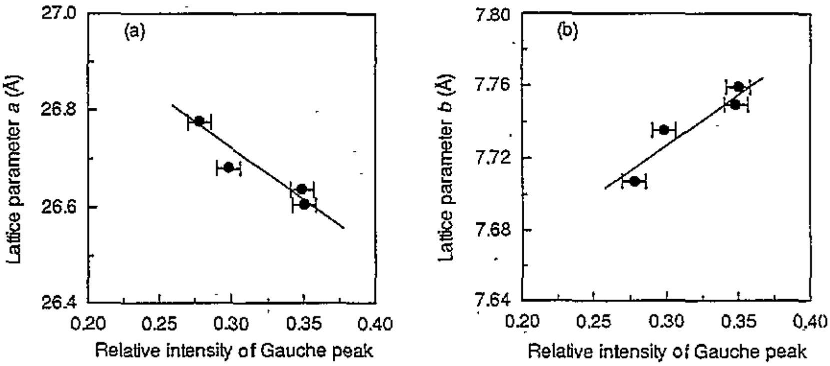

Figure 8. Plots of lattice parameters a and b against the relative intensity of the absorption peak at 1304 cm^{-1} measured several days after heat treatment at various temperatures.

These results of the FTIR measurements indicate that the considerable amount of *gauche* conformation induced by the heat treatment in the side alkyl chain does not disappear completely in the cooling process which lasts for several hours and still some *gauche* components remain in the P3DT film even after the heat treatment. Since most carbon–carbon bonds in the side chain are in the *trans* conformation, the steric hindrance of the side chain on the main chain structure should be very small and the coplanarity of the conjugated main chain and band-gap energy are not affected by the remaining *gauche* conformation. It takes several days for the release of the distortion in both the orthorhombic lattice of P3DT and the conformation of the alkyl chains. That is, in the period of several days after the heat treatment, the *gauche* structure induced in the alkyl chain relaxes to the *trans* conformation accompanying lattice relaxation, resulting in a slowly increasing relaxation of the electrical conductivity.

In conclusion, the slow relaxation phenomena in the electrical conductivity observed in the thermal hysteresis of P3DT can be attributed to the change in the lattice structure of P3DT but not to the structure of the conjugated main chain. The residual *gauche* conformation in the alkyl side chain remaining after heat treatment and its relaxation to the *trans* conformation are thought to be one of the origins of these anomalous thermal effects on the properties of P3DT. Similar results in the relaxatoin of the electrical conductivity and structure were also confirmed in other P3ATs with different alkyl chain lengths.

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