Hysteretic Thermochromism of Regioregular Poly(3-alkylthiophene) Thin Films

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ABSTRACT: We have synthesized regioregular poly(3-alkylthiophene) (P3T-HT) with different lengths of alkyl chains (C_nH_{2n+1}; $n = 4, 8, 14, 20$) attached to the polymer backbones. The chain-length-dependent thermochromic behavior was investigated by measurements of visible exciton absorption, photoluminescence, and IR vibrational absorption spectra. Optical spectra in ordered P3T-HT thin films show the nearly identical one-dimensional exciton state irrespective of the alkyl chain length, while the hysteretic thermochromic transition temperature decreases with the increase in the length. Upon the thermochromic phase transition, the order−disorder conformational change of alkyl chains occurs in a manner correlated with the conjugation length change of polythiophene backbone structures.

1. Introduction

Among many organic materials, π-conjugated polythiophenes[1] and oligothiophenes[2] derived from the thiophene moiety have been found to have interesting and unique properties such as electroluminescence, high charge carrier mobility, and third-order optical nonlinearity. In most cases, polythiophenes are insoluble in common organic solvents. By introducing the alkyl chain into 2- and/or 5-positions of the thiophene moiety, the poly(alkylthiophene) can be rendered soluble in common organic solvents, which ensures the fabrication of highly organized thin films. In addition, the π-conjugated linear backbone structure coupled with side groups of the alkyl chain provides unique optical properties such as thermochromic phase transition. In fact, reversible thermochromic behavior has been observed in many π- or σ-conjugated polymers such as polythiophene,[1,3] polydiacetylene,[4−6] and polysilane[7,8] with the substituents of alkyl chains.

Regioregular conjugated polymers have been a recent topic of interest in polymer science. In conventional cases, poly(3-alkylthiophene) (P3T) has been synthesized using the chemical oxidizing reagent and the electrochemical method, which leads to random coupling at the 2- and 5-positions of thiophene. Recently, the regioregular poly(3-alkylthiophene) (P3T-HT) has been synthesized by coupling of 3-alkylthiophene selectively using a nickel catalyst[9,10] and a Rieke zinc.[11,12] The regioregularity influences electronic and optical properties of P3T. In fact, the electrical conductivity for the regioregular P3T-HT, when carrier-doped, is enhanced more than 2 orders of magnitude as compared with the random one.[9,12,13] The charge carrier mobility can be also enhanced by increasing the regioregularity of polythiophene.[14]

In this work, we have synthesized a series of regioregular poly(3-alkylthiophene)s with different alkyl chain lengths (P3T-HT): poly(3-butylthiophene) with $n = 4$ (PBT-HT), poly(3-octylthiophene) with $n = 8$ (POT-HT), poly(3-tetradecylthiophene) with $n = 14$ (PTDT-HT), and poly(3-eicosylthiophene) with $n = 20$ (PEIT-HT). Thermochromic behaviors for all P3T-HT were investigated by measurements of visible absorption and photoluminescence spectra. Optical spectra have revealed that the phase transition temperature decreases with the increase in the chain length. On the basis of the present data, a photoinduced phase transition between the spectroscopically distinct two phases has been demonstrated in our previous paper for PEIT-HT thin films with the lowest transition temperature.[15] In the present paper, we investigate comprehensively an effect of the alkyl chain length on the hysteretic thermochromic transition. The interplay between the structural change of the alkyl chains attached to the polythiophene backbones and the thermochromic electronic change on the polymer backbone has also been investigated by measurements of IR vibrational absorption spectra.

Table 1. Characterization of P3T-HT

	C_nH_{2n+1}	M_w	M_w/M_n	T_1 (K)	T_2 (K)	ΔH (kcal/mol)
PBT-HT	4	1.94×10^4	1.71	548	500	0.4
POT-HT	8	2.94×10^4	1.61	483	445	0.6
PTDT-HT	14	3.94×10^4	1.58	428	391	0.8
PEIT-HT	20	3.36×10^4	1.57	400	370	1.5

2. Experimental Section

Sample Preparation. A regioregular poly(3-alkylthiophene) (P3T-HT) with different alkyl chain length was synthesized by the cross-coupling method using Ni catalyst.[10] The NMR analysis confirmed that all the polythiophenes show more than 99% head-to-tail (HT) couplings. The molecular weights of P3T-HT relative to polystyrene standards were determined by gel permeation chromatography. The weight-average molecular weight (M_w) of the respective P3T-HT is summarized in Table 1.

Differential scanning calorimetry (DSC) unraveled the phase transition of P3T-HT. The measurements were performed on powder (10−15 mg) of P3T-HT, which was sealed in a silver pun. For the DSC measurements, the heating or cooling rates were typically 5 K min^{-1}. The endothermic (T_1) and exothermic (T_2) peaks with an enthalpy change (ΔH) were

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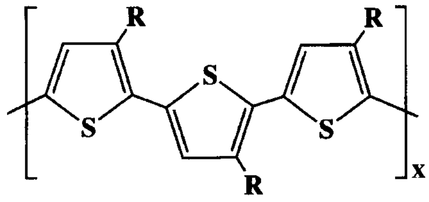

P3T-HT

$R = C_nH_{2n+1}$

C_4H_9 (n=4) : PBT-HT
C_8H_{17} (n=8) : POT-HT
$C_{14}H_{27}$ (n=14) : PTDT-HT
$C_{20}H_{41}$ (n=20) : PEIT-HT

Figure 1. Chemical structures of regioregular poly(3-alkylthiophene) (P3T-HT) used in this study.

observed in the heating and cooling runs, respectively, for P3T-HT powders. The results are summarized in Table 1.

Solid thin films of P3T-HT were prepared by spin-coating of chloroform solutions onto quartz or KBr substrates. Measurements of visible–infrared absorption and photoluminescence spectra were performed on the thin films which were annealed at a constant temperature above T_1 indicated in Table 1 under Ar atmosphere to make the backbone conformation of polythiophene further regular.

Characterization. Visible absorption spectra of the thin films were measured by using a premonochromatized light from a halogen lamp. The photoluminescence measurement was carried out with 2.58 eV light from a xenon lamp as an excitation source. The FT-IR spectra were recorded using a Nicolet model 740 FT-IR spectrophotometer equipped with a liquid nitrogen-cooled MCT detector. A resolution of each spectrum was 1 cm^{-1}. During all optical measurements, the temperature of the thin film was controlled within ±1 K.

3. Results and Discussion

Temperature Dependence of Exciton Absorption Spectra. We investigated the variation of the thermochromic behavior with the length of alkyl chains attached to the polythiophene skeleton. Figure 2 shows the temperature dependence of absorption spectra of the P3T-HT thin film with different alkyl chain lengths. There are common features in absorption spectra of POT-HT, PTDT-HT, and PEIT-HT thin films at 300 K: Well-resolved peak structures are observed around ca. 2.2 eV which can be assigned to the ^1B_u exciton band (2.0 eV) and its vibronic (C=C stretching vibration) sidebands.[16] Such distinct structures were not observed in the absorption spectra of random poly(3-alkylthiophene), which was synthesized by the $FeCl_3$ or electrochemical method. The sharp excitonic feature is due to the highly regioregular conformation of polythiophene backbones. Furthermore, the peak positions of the exciton bands were identical, irrespective of the alkyl chain length. This indicates that the backbone structure for P3T-HT has the same conformation independent of the alkyl chain length, because the spectral profiles are sensitive to the electronic structure as described below.

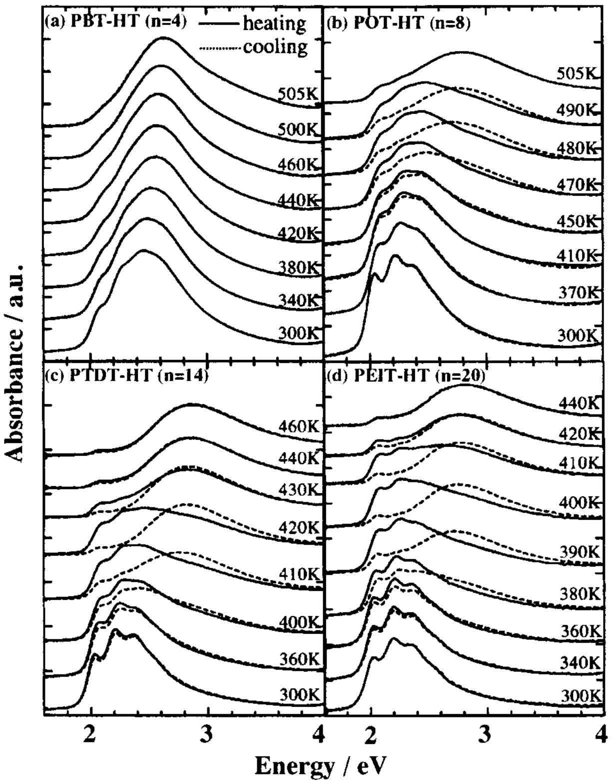

Figure 2. Temperature dependence of absorption spectra in P3T-HT thin films: (a) PBT-HT ($n = 4$), (b) POT-HT ($n = 8$), (c) PTDT-HT ($n = 14$), and (d) PEIT-HT ($n = 20$). Solid and dotted lines show the spectra in heating and cooling runs, respectively.

A similar change in the absorption spectra in heating run is observed for POT-HT, PTDT-HT, and PEIT-HT thin films. As the temperature increases, the lowest exciton absorption bands shift to higher energy, indicating a decrease in the electron delocalization (conjugation length) along the polythiophene backbone. In addition, the spectral profile with sharp structures changes into a broad one with a peak at 2.76 eV, which is probably due to inhomogeneous broadening by distribution of conjugation lengths. These results indicate that the phase transition accompanying an order–disorder conformational change of polythiophene backbones occurs at an elevated temperature. All these P3T-HT thin films show reversible thermochromic phase transition. The absorption spectra with sharp excitonic peaks were restored by lowering again the temperature for all the films, indicating that the disordered polythiophene conformation is reverted to the ordered one. Similar phase transition phenomena have been also reported in the solution of regioregular poly(3-dodecylthiophene)[17] and in π-conjugated polydiacetylenes[4–6] and σ-conjugated polysilanes.[7,8]

To clarify the nature of the phase transition accompanying the order–disorder conformation change, the intensity of the exciton absorption band at 2.0 eV was measured as a function of temperature in heating and cooling runs for the respective P3T-HT thin films, as shown in Figure 3. The POT-HT, PTDT-HT, and PEIT-HT thin films exhibit a clear thermal hysteresis. As the alkyl chain length increases, the temperature for the order–disorder phase transition decreases and the hysteretic temperature region becomes larger. The transition between the two phases is also confirmed by measurements of the differential scanning calorimetry (DSC) thermogram. Respective phase transition temperatures as revealed by optical measurements well correspond to the temperatures of the endothermic and exothermic peaks (T_1 and T_2) of the DSC thermogram, respectively (see Table 1), for all the P3T-HT investigated.

There is a clear difference in a spectral feature and thermochromic behavior of absorption spectra between

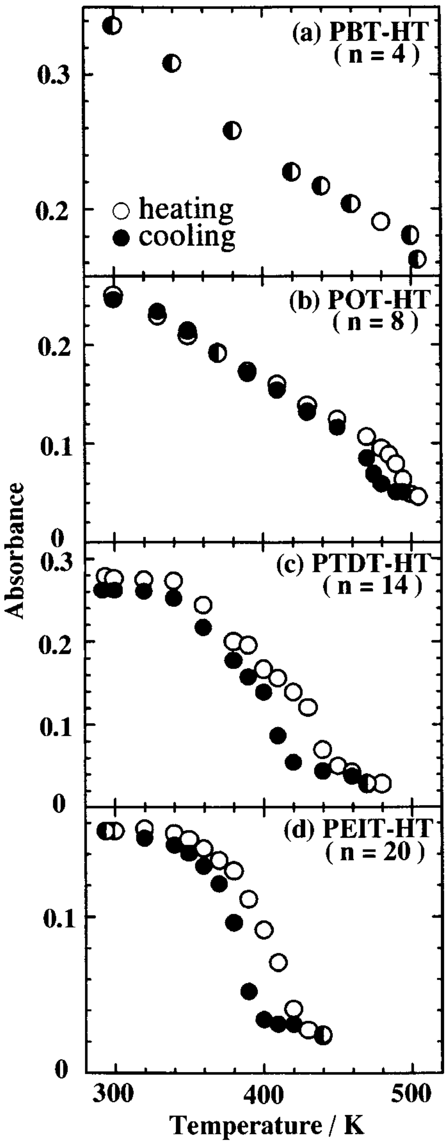

Figure 3. Change in the peak intensity of exciton absorption at 2.04 eV as a function of temperature in P3T-HT thin films: (a) PBT-HT, (b) POT-HT, (c) PTDT-HT, and (d) PEIT-HT.

the PBT-HT and the other ones. The absorption bands assigned to the lowest exciton band with the vibronic sidebands are also discernible in PBT-HT thin films, but the spectral profile becomes broader than those of other P3T-HT thin films. The PBT-HT probably does not form highly regular conformation of polythiophene backbones. On heating, the lowest exciton absorption bands shift to higher energy and become broader as the temperature is elevated. Compared with the change of absorption spectra in heating and cooling runs for the other P3T-HT thin films, however, a clear phase transition due to order−disorder conformation change was not observed below 505 K, which is the highest temperature attained in this study. In DSC measurements of PBT-HT powder, the endothermic peak was observed at 548 K (over 505 K) in the heating run. The spectroscopic change due to the phase transition would be observed by heating PBT-HT thin films to higher temperature.

In the following, we focus on the spectroscopic change upon the phase transition of PEIT-HT thin films whose phase transition temperature is the lowest among four P3T-HT's investigated in this study.

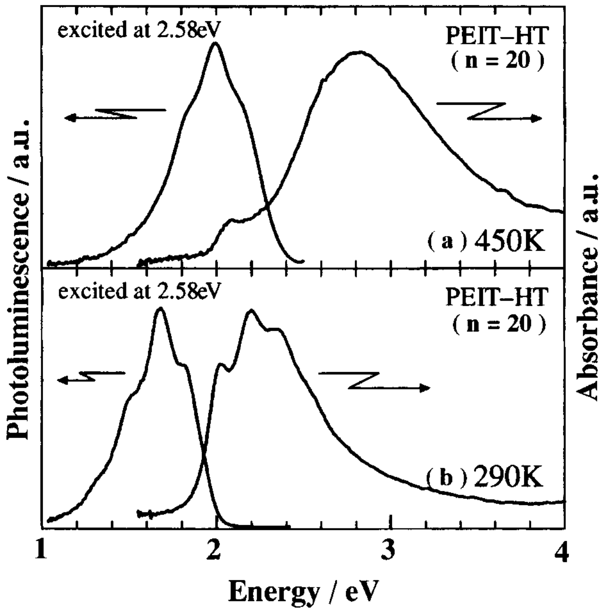

Figure 4. Photoluminescence and absorption spectra in PEIT-HT thin films at 290 K (a) and 450 K (b).

Temperature Dependence of Photoluminescence Spectra. Figure 4 shows photoluminescence spectra of the PEIT-HT thin films at 290 and 450 K. For comparison, the absorption spectra at respective temperatures are also shown in Figure 4. The PL spectrum at 290 K shows a zero-vibronic band at 1.8 eV followed by the sidebands, which shows an approximate mirror image to the absorption spectrum. The energy difference between the zero-vibronic bands of absorption and PL spectra, that is, Stokes shift, is 0.2 eV. Upon the phase transition, the absorption spectra become broad, reflecting the disorder of the polythiophene conformation, but the PL spectrum shows a similar profile accompanying the vibronic sidebands though the zero-vibronic band shifts to higher energy. This indicates that the radiative decay of the photogenerated excitons probably occurs at the most conjugated segments of the polymer chains after the exciton migration, while the absorption spectrum reflects the average of the polymer backbone segments.

Figure 5 shows temperature variation of the PL spectra for the PEIT-HT thin film (in a heating run). Upon the order-to-disorder phase transition, the PL intensity was observed to be remarkably enhanced. In the inset of Figure 5, the PL intensity at 2.15 eV, which corresponds to the zero-vibronic bands in the disorder phase, is plotted as a function of temperature. The behavior shows a clear hysteresis as well as that of the absorption spectra (see Figure 3d).

Structural Change upon the Phase Transition. To clarify a conformational change of the alkyl chains upon the phase transition, we measured infrared vibrational spectra of a PEIT-HT thin film. Figure 6 shows the FT-IR absorption spectra in the CH stretching region as a function of temperature (in a heating run). Two sharp and intense bands are observed at 2851 and 2919 cm^{-1} at 295 K, which are assigned to the CH$_2$ symmetric (ν_s(CH$_2$)) and asymmetric (ν_{as}(CH$_2$)) stretching band, respectively. These band positions and the spectral profiles are known to be sensitive to the change in the packing of the alkyl chains.[18−20] Upon the phase transition to the disordered conformation of polythiophene backbones, the spectral profile of the two

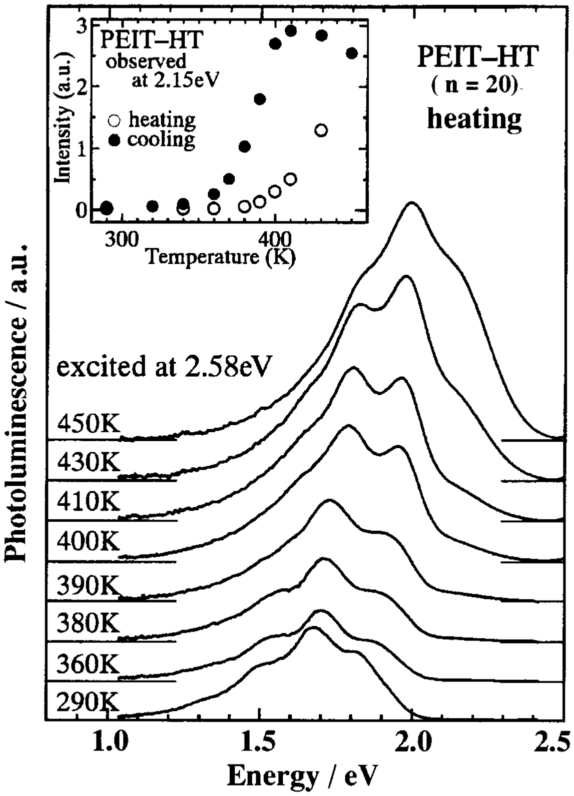

Figure 5. Temperature dependence of photoluminescence spectra in PEIT-HT thin films. The inset shows the change in the intensity of a photoluminescence peak at 2.15 eV.

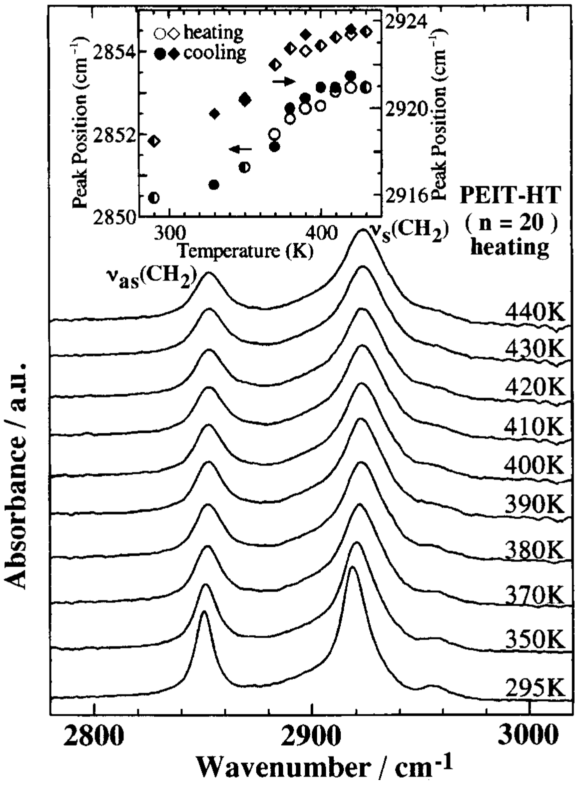

Figure 6. Temperature dependence of the infrared absorption spectrum in PEIT-HT thin films. The inset shows the change in the peak position of the $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ stretching bands.

bands for the alkyl chains becomes broader. In the inset of Figure 6, the temperature variation of the two peak positions, $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$, is plotted. A hysteresis behavior was barely discernible, but both modes shift to higher wavenumber with heating. These results suggest that the packing of the alkyl chains attached to the polythiophene backbone changes from the trans zigzag conformation to the disordered one upon the phase transition. The peak position and the spectral profile characteristic of disordered alkyl chain at high temperature are reverted to the initial ones when the PEIT-HT thin film is cooled to room temperature. Therefore, the reversible thermochromic phase transition of polythiophene conformation is coupled with the order–disorder transition of alkyl chains.

4. Conclusion

Regioregular poly(3-alkylthiophene) (P3T-HT) with varying alkyl chain length was synthesized. One-dimensional exciton structures in the low-temperature phase of the polymer backbones are common to all the regioregular polymers irrespective of the alkyl chain length. We have investigated the thermochromic behaviors for all the P3T-HT thin films by measurements of visible absorption and photoluminescence spectra. The transition temperature decreases with the increase of the chain length. The zero-vibronic band accompanied by vibronic sideband structures was observed in the photoluminescence spectra. The luminescence intensity increases several times upon the transition to the high-temperature phase. From the results of temperature dependence of IR transmission spectra, we have demonstrated that the thermochromic phase transition between the two forms is coupled to the order–disorder transitions of alkyl chains.

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