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The Optical Signatures of the Temperature Controlled Order-Disorder Conformational Transition during the Aggregation Processes in Poly (3-Hexylthiophene-2, 5-Diyl) (P3HT) Thin Films

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Abstract

Π-conjugated polythiophenes and oligothiophenes derived from the thiophene moiety have been reported to have unique properties such as electroluminescence, high charge carrier mobility, and third-order optical nonlinearity. Thermochromism in various regioregular and non regioregular polythiophene derivatives have been investigated both in the solid state and in solution and have revealed a first-order-like conformational transition of the conjugated backbone (formation of twisting) which leads to important colour changes. The structural evolution of the P3HT in thin films or solutions can be inferred from optical spectroscopic measurements during the polymer crystallization (ordering) process. Properties such as conjugation length, intermolecular coupling within the aggregates and the packing behaviour of the polymer chains as well as the presence of defects can be studied carefully during this process. From this study, we use the temperature dependent interplay of the vibronic peaks to infer the intra and inter-chain cross-talks in P3HT thin films. We thus report thermally induced cooperative conformational transition of the polymer main chains during the thermally induced structural evolution.

Keywords: Absorbance; Photoluminescence; Excitonic coupling; Twistons; Conjugation length; Excitonic bandwidth; Vibronic peaks

Introduction

Thermochromism which is the reversible change in colour of a substance due to temperature change is a common phenomenon in regioregular π-conjugated polymers [1-6]. These unusual optical effects are believed to be related to a reversible “transition” in planarity of the conjugated main chain [8]. It is an academic task to answer the questions on the reasons for thermo chromic behaviour in π-conjugated systems i.e. whether they are driven by intrachain conformational changes or by interchange interactions. Since thermo chromic changes are always accompanied by an increase of interchange interactions, the detection of temperature-dependent absorption changes in thin films is a suitable tool to gain insight into the factors that controls the π- π stacking phenomena of the conjugated polymer chains. Interestingly, the detection of temperature-dependent absorption changes in thin films can be used to gain insight into the factors that controls the π- π stacking phenomena of the polythiophene chains. Over a given time, absorption and PL spectra of poly (3-hexylthiophene) (P3HT) have been described in terms of intramolecular interactions coupled to only a single photonic mode [8-13]. However, Brown et al. has shown that for highly organized/ordered P3HT thin films and crystals, this model has been shown to be simplistic and cannot satisfactorily describe the spectra due to the presence of both the intramolecular and intermolecular couplings showing up in the absorption and emission spectra. The absorption spectra of rrP3HT thin films spun from different solvents have been shown to be composed of two parts; a lower energy part, dominated by the better crystalline absorption (interchange states) and a higher energy part due to more disordered chains which form the intrachain states [14-16]. The number and the nature of the P3HT aggregates are of key roles for their optoelectronic applications. Formation of aggregates in P3HT thin films depends on molecular weight, solvent, regioregularity and synthetic method just to mention but a few. It is thus important to investigate the temperature dependent formation kinetics of P3HT thin films.

Experimental

Materials and equipment

For all the experiments presented in this article, Merck KGaA under the Lis icon® brand Poly (3-hexylthiophene) (P3HT-24) of molecular weight (Mw) 24480 gmol-1, Regularity 93.6% and disparity index (DI=Mw/MN) of 2.8 has been studied. UV-Vis absorption spectroscopy measurements were performed using the Shimadzu Parma Spectro-1700 series spectrophotometer. 20 W halogen lamp and deuterium lamp with a wavelength range of 190 to 1100 nm light sources were used for excitation for absorbance measurements. For the substrates, we used glass. The heating and cooling of the samples was achieved by the use of silicon bath for solution and hot stage purged with nitrogen for thin films.

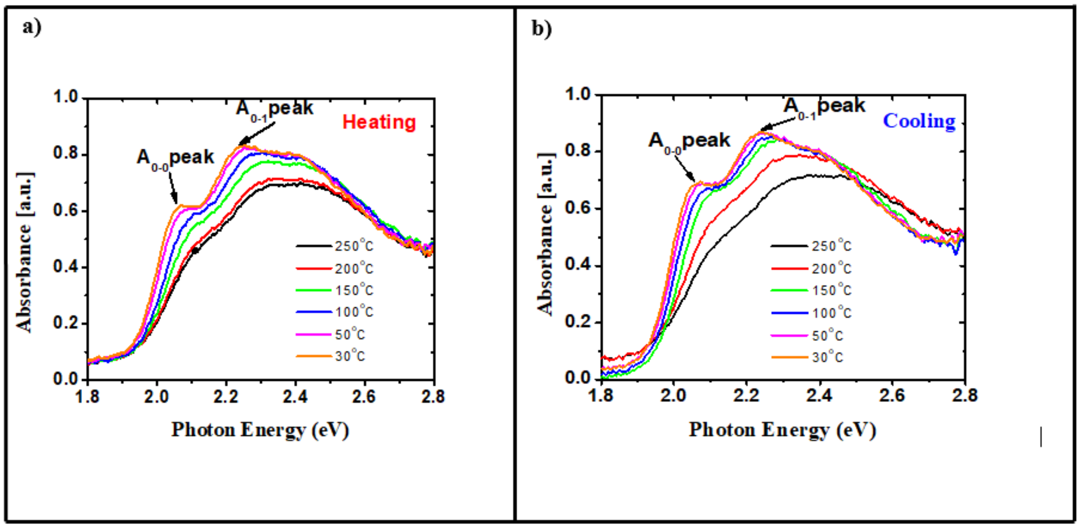
Experimental Procedure

The P3HT-24 aggregates reported in this study were prepared via homogeneous nucleation process. P3HT-24 solutions of concentration $0.3 gL^{-1}$ were prepared in toluene solvent at a temperature well above maximum dissolution temperature (Tdiss, max=75°C) for 30 minutes to fully dissolve the polymer. Temperature dependent optical absorbance spectra were again collected from thin films prepared by spin casting 2 μL of the solutions of P3HT-24 solutions on glass substrates at 1000 rpm for 2 minutes followed by a vacuum oven drying for 2 hours to completely remove the residual solvents. The spectra were collected at 30°C, 50°C, 100°C, 150°C, 200°C and 250°C during the film heating and cooling processes using the Shimadzu Parma Spectro-1700 series spectrophotometer.

Results

From the spectrographs, it is clear that as the temperature increases, the lowest exciting absorption bands shift to higher energy, indicating a decrease in the electron delocalization (conjugation length) along the polythiophene backbone (Figure 1). The converse happens during the cooling processes.

Figure 1: *The absorbance spectra of P3HT-24 thin film during heating (a) and cooling (b). There is blue shifting of the highest absorption band during heating and red shift of the band during the cooling process.*



Discussion

Temperature dependent order-disorder transition in thin films

Spin coating of the polymer solutions provides thin films with the expected shift of the π-π* transition with respect to the solution state spectra due to increased planarity of the conjugated backbone in the solid state. As has been discussed, the degree of coupling between chains manifests itself in the absorbance spectra as the ratio of the lowest energy peak (A_{0-0}) and next replica peak (A_{0-1}) heights. An increase in the A_{0-0}/A_{0-1} peak ratio with decrease in temperature corresponds to a decrease in the excitonic coupling, therefore an increase in the conjugation length and intrachain order (Figure 2). Also observed was a slight red-shift of the progression peaks indicating high conjugation length. All

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these P3THT thin films show reversible thermo chromic phase transition. However, the absorption spectra with sharp excitonic peaks are restored by lowering again the temperature for all the films, indicating that the disordered polythiophene conformation is reverted to the ordered one.

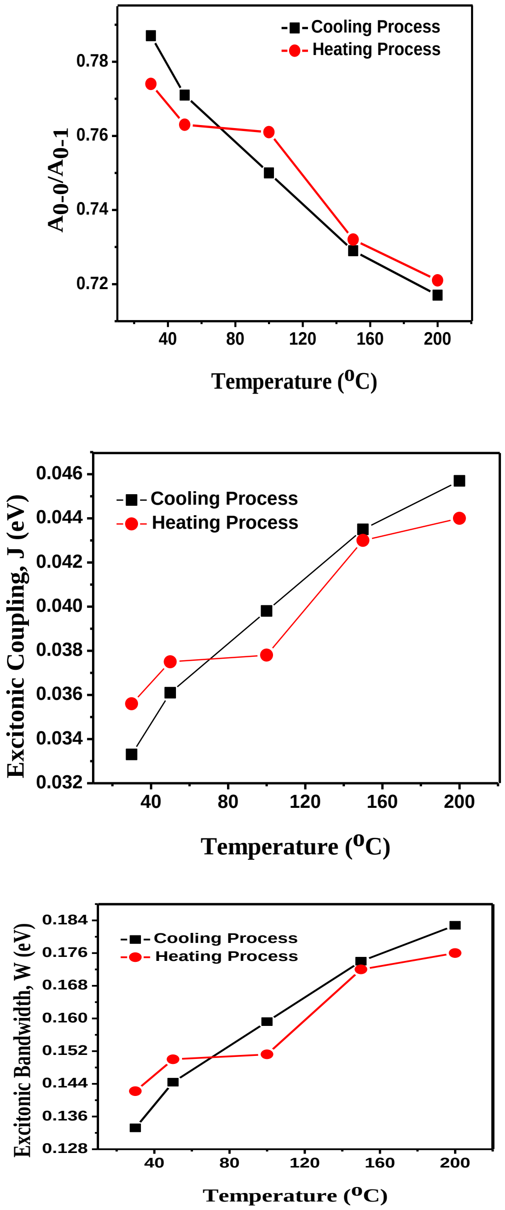

Figure 2: *Graphs of the oscillator strength ratios $A_{0\text{-}0}$ / $A_{0\text{-}1}$ (a), the excitonic coupling, J (b) and the excitonic bandwidth W (c) as functions of temperature during the thin film cooling and heating processes.*

Solution-thin film order-disorder transition in P3HT-24

We further compared the P3HT-24 nanofibers in solution and in thin film. The absorbance spectra ratio of the lowest energy peak ($A_{0–0}$) and next replica peak ($A_{0–1}$) heights $A_{0–0}/A_{0–1}$=0.891 for thin films and $A_{0–0}/A_{0–1}$=0.727 for aggregated solution are shown in (Figure 3). This suggests decreased excitonic coupling and increased conjugation length and intrachain order in thin films than in solution. Also observed was a slight red-shift of the progression peaks for P3HT-24 in thin films indicating high conjugation length and better structural order.

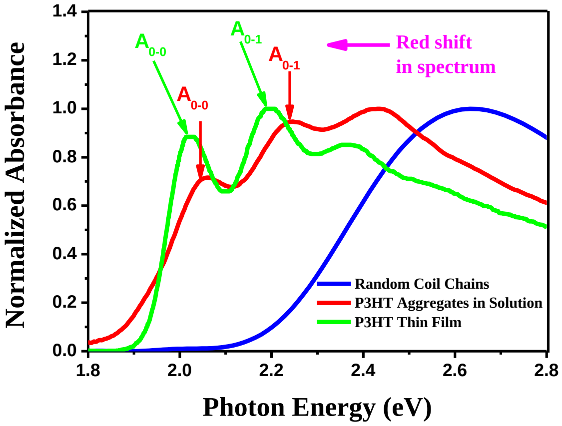

Figure 3: *The absorbance spectra of P3HT-24 fully dissolved in solution, aggregates in solution and thin film.*

Conclusion

The optical measurements have revealed a first-order-like conformational transition of the conjugated backbone (formation of twisting). Furthermore, reversible thermally induced cooperative conformational transition of the main chain has been observed. This has been corroborated by the reversibility of the oscillator strength ratios $A_{0\text{-}0}$ / $A_{0\text{-}1}$, the excitonic coupling, *J*, and the excitonic bandwidth *W* during the heating and cooling processes.

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