

COMPARISON OF ANALYTICAL METHODS FOR CHARACTERIZATION OF THE THERMOCHROMIC TRANSITION OF POLY(3-ALKYLTHIOPHENE)S

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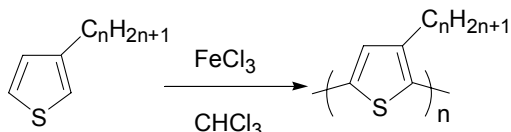
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Introduction

Conjugated polymers have received extensive investigation over the past two decades due to their interesting conductive and semi-conductive properties. These polymers have been utilized for a variety of electronic applications including light emitting diodes, electrochromic materials, and sensors.¹ Another interesting property of many conjugated polymers is thermochromism. The change in color of the conjugated polymer as a function of temperature is reported to result from conformational changes in the polymer backbone, which results in a shortening of the effective conjugation length of the polymer. The thermochromic transition is typically accompanied by a phase transition. Thermochromic transitions have been reported for substituted polythiophenes,² polydiacetylenes,³ and poly(*p*-phenyleneethynylene)s.⁴ Investigations of the thermochromic transitions of poly(3-alkylthiophene)s have utilized variable temperature absorption, emission, and infrared spectroscopy, differential scanning calorimetry, and X-ray diffraction to characterize the phase transition. However, most investigations primarily rely upon optical absorption spectra. The most frequently utilized method for illustrating the thermochromic transition is a plot of the λ_{\max} as a function of temperature. However, this illustration does not provide the best depiction of the phase transition responsible for the color change. We have been investigating alternative analytical techniques for the depiction of the thermochromic transition.

Experimental

Preparation of regiorandom poly(3-alkylthiophene)s. Poly(3-alkylthiophene)s were synthesized from the corresponding 3-alkylthiophene via oxidative polymerization with FeCl_3 (Scheme 1).⁵ The structures of the polymers were confirmed by ^1H and ^{13}C NMR spectroscopy and the polymer molecular weights were estimated by gel permeation chromatography.



Scheme 1. Synthesis of poly(3-alkylthiophene)s.

Optical absorption measurements. Thin films of poly(3-alkylthiophene)s were cast on quartz cuvettes from THF solutions passed through a 0.22 micron filter. The samples were heated to remove residual solvent before variable temperature spectroscopic analysis.

Results and Discussion

UV-visible absorption spectra for a series of poly(3-alkylthiophene)s (Scheme 1, $n = 12, 13, 14, 16, 17, 18, 20$) were acquired between room temperature and 100°C . Variable temperature UV-visible absorption spectra of regiorandom polythiophenes substituted with long alkyl substituents ($n > 12$) are reported to include an isosbestic point.⁶ This suggests that poly(3-alkylthiophene)s have two phases, an ordered low temperature phase and a disordered high temperature phase. A thorough investigation of the thermochromic transition will provide a better understanding of the phase transition in poly(3-alkylthiophene)s. In particular, how the length of the alkyl side chain effects the temperature breadth of the transition (ΔT) and the middle temperature of the transition (T_m). The variable temperature absorption spectra and corresponding thermochromic transitions have been analyzed by four different methods; λ_{\max} , low energy band edge, first moment, and the color of the film as defined by the CIE coordinates. While most of these methods have not been utilized for the characterization of the

thermochromic transition of conjugated polymers, colorimetric analysis has recently been utilized for the characterization of the electrochromic properties of conjugated polymers.⁷

Investigation of the λ_{\max} of the optical absorption as a function of temperature indicates a general shift of the optical absorption (Figure 1). While this is the most frequently used method we obtained little information on either ΔT or T_m from the plot. However, the absorption spectra reveal a clear isosbestic point and the change from red to yellow occurs over a small (30°C) temperature range.

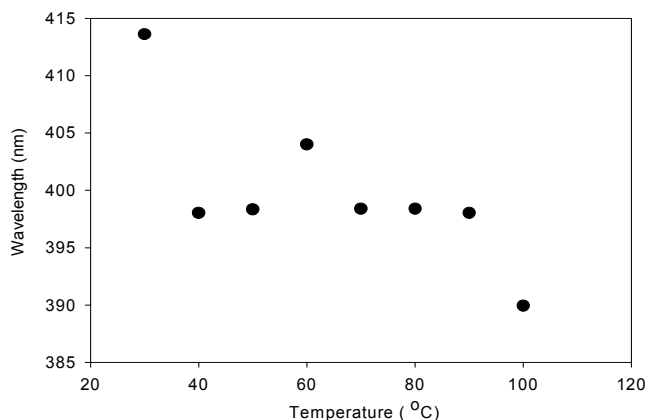


Figure 1. Plot of the λ_{\max} of the optical absorption of poly(3-heptadecylthiophene) vs. temperature.

Investigation of the low energy band edge of the optical absorption as indicated by the wavelength at half maximum vs. temperature provides a significantly improved depiction of the thermochromic transition (Figure 2). The data is easily fit to a sigmoidal function, as expected for a two phase transition, allowing a quantitative measure of both ΔT and T_m . This allows an accurate comparison of both ΔT , the domain of temperature change, and T_m , the inflection point for poly(3-alkylthiophene)s with different alkyl side chains. Investigation of both the center of integrated absorbance intensity and color also provide better depictions of the thermochromic transition than the λ_{\max} of the optical absorbance.

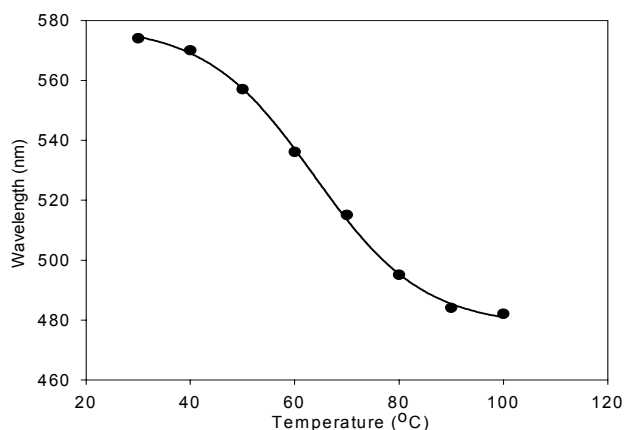


Figure 2. Plot of the low energy band edge of poly(3-heptadecylthiophene) vs. temperature.

Our investigation of the phase transition accompanying the thermochromic transition in poly(3-alkylthiophene)s includes differential scanning calorimetry and infrared spectroscopy. Through this thorough analysis we will gain a detailed understanding of the structural changes that result in the thermochromic transition of poly(3-alkylthiophene)s.

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