INVESTIGATION OF THE THERMOCHROMIC PROPERTIES OF POLYTHIOPHENES DISPERSED IN HOST POLYMERS

Brett L. Laucht, William B. Euler, and Otto J. Gregory

Departments of Chemistry and Chemical Engineering
University of Rhode Island
Kingston, RI 02881

Introduction
There have been numerous investigations of the structure and organization of polythiophene films and the structural changes that occur during the thermochromic transition. The investigations have primarily focused on the behavior of these materials as pure films or in solution. However, the utilization of conjugated polymers in many electronic applications requires them to be dispersed in a host polymer matrix. There have been few investigations on the thermochromic properties of polythiophenes in host polymers. In this article we discuss an investigation of the structure and organization of substituted polythiophenes as pure solids and as dispersions in host polymers. The polymers of most interest include polystyrene, poly(methyl-methacrylate), polycarbonate, and polyolefins.

Experimental
Preparation of regiorandom poly(3-alkylthiophene)s. Poly(3-alkylthiophene)s were synthesized from the corresponding 3-alkylthiophene via oxidative polymerization with FeCl3 (Scheme 1). The structures of the polymers were confirmed by 1H and 13C NMR spectroscopy and the polymer molecular weights were estimated by gel permeation chromatography.

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.

Thermal analysis. DSC measurements were made on a TA instruments DSC Q100 with refrigerated cooling system.

Microscopy. Optical microscope images were obtained on a Nikon Type 4 optical microscope. Scanning Electron Microscope images were obtained on a JEOL JSM-5900.

Results and Discussion
Mixtures of structurally distinct polymers typically phase separate in the solid state. The behavior of the polymer mixture is dependent upon this phase segregation. We are interested in determining the size of the substituted polythiophene aggregates and the degree of order within the aggregate. We have used a variety of surface and solid state analytical techniques, as described below, to investigate the polythiophene dispersions. The analytical techniques allow us to determine the size of polythiophene particles in the host polymer, the degree of order, and thermodynamic aspects. A firm understanding of the structure of the polythiophene phases in the host polymer will help us to understand differences in the thermochromic properties of transition in host polymers and in neat films.

The generally accepted mechanism for the thermochromic transition is based on a two-step process. At low temperature the polymer has the conjugated repeat units (responsible for the color) in a planar conformation and the substituents of the polythiophene chain ordered into a lattice. As the temperature is raised, the side chain lattice melts and the resulting disorder allows the main chain repeat units to twist away from planarity (Scheme 2). The twisting of the polythiophene units increases the band gap, resulting in a blue shift of the optical absorption (Scheme 3). Polythiophenes with long sidechains are believed to have sharp thermochromic transitions due to the two phase morphology. The melting of the sidechains causes a zipper effect which results in a sharp thermochromic transition. The observation of a clear isobestic point in the variable temperature UV-Visible spectra (Figure 1) supports this two-phase model. However, the mechanism of the thermochromic transition in host polymers has received little attention.

![Scheme 1. Synthesis of poly(3-alkylthiophene)s.](image)

![Scheme 2. Polythiophene side chain melting.](image)

![Scheme 3. Polythiophene backbone conformational change.](image)

![Figure 1. Variable temperature UV-Visible spectrum of poly(3-alkylthiophene).](image)

The thermochromic transition can be used to monitor the phase transition occurring in the polymer structure. Plots of the band edge at half of the wavelength maximum for poly(3-alkylthiophene)s with sharp thermochromic transitions, characteristic of two phase transitions, can be fit to a sigmoidal function providing a mathematical fit (Figure 2). The mathematical fit provides a well-defined measurement for both the middle temperature (T_m) and the range of the thermochromic transition (ΔT).

Preliminary investigations reveal different structures in different host polymers. Optical microscopy of polycarbonate chips with 0.5 % poly(3-alkylthiophene) indicates polythiophene aggregates ranging from 5 to 50 μm in diameter. The size of the polythiophene aggregates was confirmed by SEM (Figure 3) while the presence of sulfur in the aggregates was confirmed by EDX. The structure is quite different in polyethylene and polypropylene. We were unable to observe any evidence for polythiophene aggregation by optical microscopy and SEM at the same magnification as used for the polycarbonate samples (Figure 2). Investigation of the polyethylene and polypropylene chips with SEM at a magnification of 10,000x was unable to uncover any evidence for polythiophene aggregation. This suggests a maximum diameter of 50 nm for the aggregates. The thermochromic response of poly(3-alkylthiophene) is identical in both polycarbonate and polyolefins despite a decrease in the diameter of the
aggregates by at least three orders of magnitude. This places into question the mechanistic dependence of thermochromism on aggregation.

Figure 2. Plot of the low energy band edge vs. temperature for a poly(3-alkylthiophene) film.

Figure 3. SEM Images of 0.5 % polt(3-alkylthiophene) in polycarbonate (top) and polyethylene (bottom).

Preliminary thermal analysis of solid poly(3-alkylthiophene) by DSC indicates two distinct reproducible transitions upon heating, with related endothermic transitions observed upon cooling (Figure 4). The endothermic transition at 38 °C is believed to be associated with the disordering of the alkyl side chains while the endotherm at 65 °C is consistent with the disordering of the main chain thiophenes. The small irreversible endothermic transition at 50 °C is consistent with a loss of residual solvent. The endothermic transitions are shifted slightly upon the second heating cycle but remain constant upon additional heating and cooling cycles. We observe a related change in thermochromic response of poly(3-alkylthiophene) during the first heating which undergoes no further changes upon repeated heat cycling. The middle temperature (T_m) and the range (∆T) of the endothermic transition at 65 °C are nearly identical to those observed for the thermochromic transition as measured spectroscopically.

Figure 4. DSC curve for solid poly(3-alkylthiophene).

Conclusions
The thermochromic transition of poly(3-alkylthiophene)s occurs over a narrow region and the spectroscopic data can be fit to a sigmoidal function supporting a two-phase transition. The thermochromic transition is not altered upon dilution of the poly(3-alkylthiophene) in common plastics including polystyrene, polyolefins, polycarbonate, or poly[methylmethacrylate]. The lack of observed polythiophene aggregates by both optical and scanning electron microscopy in polyethylene suggests that the thermochromic transition may not be due to side chain melting. Differential scanning calorimetry indicates an independence of the side-chain melting and main-chain twisting. The data strongly supports the independence of side chain melting and the thermochromic transition questioning the importance of side chain melting in an aggregation model of thermochromic transitions in polythiophenes.

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References