

Reversible thermochromic effects in poly(phenylene vinylene)-based polymers

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We study the thermochromic response of poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (PPV) gel films. These films undergo a reversible, continuous color change from red to yellow in the practically relevant temperature range of 25–100 °C. We show that the absorption and photoluminescence continuously decrease and blueshift along with an increase in both highest occupied molecular orbital and lowest unoccupied molecular orbital levels as the temperature is increased, and that this effect does not depend on glass transition temperature. Understanding the changes in this widely used, versatile class of materials at elevated temperatures is important in controlling the operation of polymer photovoltaics and has implications in the fundamental factors affecting emission color in PPV based materials. © 2006 American Institute of Physics. [DOI: 10.1063/1.2183360]

Thermochromic materials, or materials that change their color depending on temperature, have been known for some time.¹ The applications for such materials include smart windows, temperature sensors, color filters, and displays. The typical organic thermochromic materials achieve color change with increased temperature through a change in crystal structure.² The discovery that conjugated polymers, which are naturally disordered in the solid state, can also undergo temperature-dependent color changes that occurred in 1988 with substituted polythiophenes.³ Polymers of this type form the bulk of the literature on thermochromic effects in conjugated polymers. A few poly(phenylene vinylene) (PPV) derivatives that display thermochromic properties have been reported.^{4–6} However, these materials suffer from low contrast at practical temperature ranges, low reversibility, or phase changes that accompany the color change, rendering them impractical for many applications.

We report a study on the thermochromic effects in the widely used light-emitting polymer (poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and in two related copolymers, (poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethynylene-2,5-dimethoxy-1,4-phenylene-ethynylene] (M3EH-PPV) (Ref. 7) and (poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethynylene-2,5-dioctyloxy-1,4-phenylene-ethynylene] (MEH-DOO-PPV) (Ref. 7). Thin gel films of MEH-PPV were formed that exhibited a striking color change from red to yellow when heated from room temperature to 100 °C. Measurements of the temperature-dependent absorption spectra, photoluminescence spectra, highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) energy levels are performed in order to quantify and interpret these effects.

The primary thermochromic species studied was MEH-PPV, provided by American Dye Source. MEH-PPV is an orange-red, luminescent polymer easily soluble in common organic solvents. Other polymers studied included M3EH-PPV and MEH-DOO-PPV provided by Horhold and Tillman.⁷ Thermochromic polymer gel films were prepared

from a solution of 0.8% polymer by weight in a mixture of chlorobenzene and dibutyl sebacate, a plasticizer, at a typical ratio of 5:1. Similar thermochromic effects were observed with pure polymer films spin cast from a solution in chlorobenzene alone but the effects appeared to be slower, slightly less reversible, and less dramatic. The solution is spin cast on untreated quartz substrates at 1000 and 3000 rpm for 30 s to achieve approximate film thicknesses of 200 and 80 nm for PL or transmission measurements, respectively. All films were dried under vacuum (10^{-6} Torr) overnight prior to testing.

In the temperature range between 25 and 100 °C, MEH-PPV films undergo a transition from red to yellow. Photographs of films taken by placing the film on a hot plate at 25, 62, 80, and 100 °C are shown in Fig. 1. After placing the film on the hot plate, the color change occurred instantly. After removing the film from the heat source its original color returned immediately upon cooling of the film. This color change appeared to be completely reversible and no volume change or phase change of the polymer film was visually observed. It is likely that the lack of observed melt-

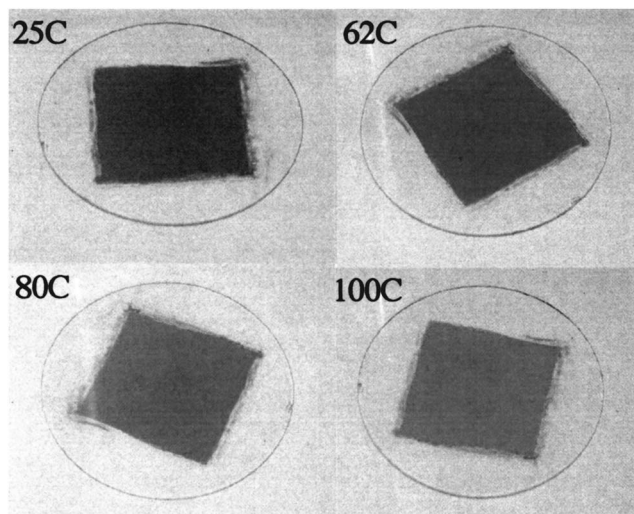


FIG. 1. MEH-PPV films at 25, 62, 80, and 100 °C.

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ing of the film, despite heating above the polymer glass transition temperature, is due to the addition of the plasticizer dibutyl sebacate which allows the film to form a more gel-like, rather than solid film at room temperature.

To understand more qualitatively the observed color change, temperature-dependent absorption spectra were obtained. Transmission spectra for thermochromic films were taken on an n&k Varian Cary 3 spectrophotometer. Samples were heated *in situ* by securing a nichrome wire against the film with a conductive tape as close as possible to the substrate center so as to avoid interference with the measurement, and passing current through the wire. The temperature was allowed to equilibrate prior to scanning, taking approximately 5–10 min depending on the step size. Heating of the film occurred through conduction in the substrate and therefore suffered a minor level of nonuniformity. However, temperatures were tested immediately prior to the scan at the film center and thus accurately correlate with the temperature of the part of the film where the transmission was measured. The high-temperature limit of such a setup appeared to be the breakdown of the tape adhesive occurring at around 80 °C.

The film absorption between approximately 25 and 80 °C for all three materials is shown in Fig. 2. As the temperature is increased the films undergo a continuous blueshift and decrease in overall absorption. The decrease in spectral weight of the absorption in the visible range is most likely compensated for by increased phonon contributions to the absorption in the infrared. The blueshift of the absorption of MEH-PPV in the temperature range of 25–80 °C was approximately 19 nm, while the blueshifts for M3EH-PPV and MEH-DOO-PPV were 17 and 14 nm, respectively.

A blueshift of the photoluminescence is also observed in MEH-PPV at increased temperature. Film heating for PL measurements was performed by placing the films on a hot plate. Figure 3 shows photoluminescence spectra and photographs of the PL of MEH-PPV at 25 and 80 °C taken using an Osram HBO-100 W/2 mercury short arc photo optic lamp with a rhodamine filter on a hot plate. No significant further blueshift is observed past approximately 80 °C in this material.

Along with an increase in the polymer effective band gap, we expect to see shifting of HOMO/LUMO energy levels. We therefore performed temperature dependent cyclic voltammetry experiments in the range 25–40 °C. Cyclic voltammetry experiments for MEH-PPV only were performed using a nonaqueous silver/silver ion reference electrode (Ag/Ag^+ , 0.3 V versus SCE), a platinum counter electrode and a spin-cast MEH-PPV/indium–tin–oxide working electrode. Solutions were 1% by weight MEH-PPV in chlorobenzene and were spin cast at 200 rpm to achieve a 50 nm film. Following polymer deposition, all substrates were annealed at 120 °C for 30 min under vacuum, and dried in a vacuum chamber ($\sim 10^{-6}$ Torr) overnight. The electrolyte consisted of 0.01 M tetrabutylammonium tetrafluoroborate in acetonitrile and was purged with nitrogen prior to testing for 5 min in order to reduce air contamination. Data were obtained on an EG&G Princeton Applied Research Model 362 scanning potentiostat and two 2010 Keithley multimeters.

The entire cell was placed on a hot plate and the temperature monitored using a thermometer. The electrolyte was allowed to reach equilibrium temperature prior to scanning.

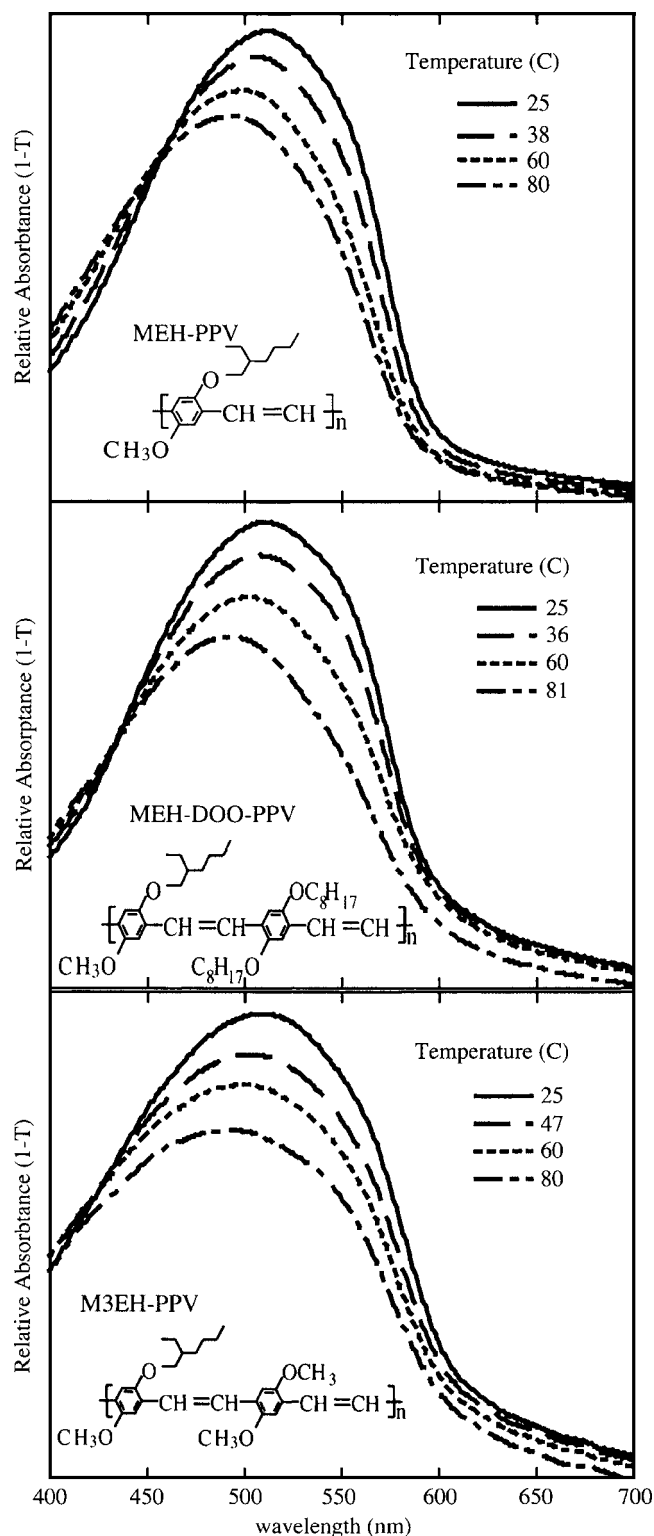


FIG. 2. Temperature dependent absorption spectra and molecular structures of MEH-PPV, MEH-DOO-PPV, and M3EH-PPV.

HOMO and LUMO levels were extracted from the *p* and *n* onset potentials as described previously.⁸ Both the HOMO and LUMO levels are increased as the sample is heated, but the LUMO shifts more dramatically, resulting in an overall increase in the band gap, consistent with the spectroscopic data. In this limited temperature range, we observed an increase in the HOMO level of 0.03 eV and an increase in the LUMO level of 0.13 eV for an overall bandgap increase of 0.1 eV. This trend is consistent with that of Onada and Tada⁶

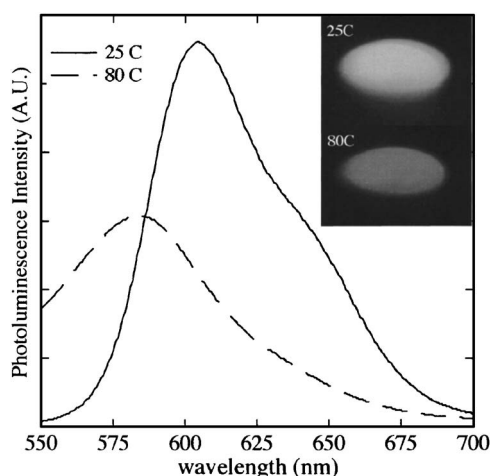


FIG. 3. MEH-PPV photoluminescence spectra and photographs of PL at 25 °C and approximately 80 °C.

who demonstrate and propose a mechanism for this trend in similar materials.

These results are consistent with the well understood mechanism for thermochromic effects in conjugated polymers first proposed in 1989.³ In this model, the polymer sidechains become bulkier with heating. Steric hinderance between in-plane sidechains forces twisting to occur in the polymer backbone. It is this conformational change in the polymer backbone that shortens the conjugation length and thus blueshifts the material absorption and photoluminescence.^{3,9} The extent of this effect should depend both on the rigidity of the backbone itself and also on the relative bulkiness of the sidechains.

The differences between MEH-PPV and the related materials M3EH-PPV and MEH-DOO-PPV were minor and illustrate that the introduction of alternating units with varying sidechain size in materials with the same backbone structure does not affect the thermochromic properties noticeably. In addition, the low glass transition temperature⁷ of MEH-PPV (65 °C) as compared with that of M3EH-PPV (108 °C) did not result in any noticeable differences in thermochromic behavior. This is not surprising, because while the shorter sidechains result in higher rigidity, they typically also result in higher rotational freedom.¹⁰ We therefore expect that for moderate changes in sidechain structure, no significant change will be observed in thermochromic properties. We can therefore also conclude that the glass transition temperature is much more sensitive to sidechain length than the ther-

mochromic effect is for these materials. It is interesting to note that the optical characteristics of MEH-PPV begin to approach those of PPV as the temperature is increased.¹¹ It is possible in light of these results that the redshift in the emission of MEH-PPV with respect to that of PPV is due in part to the fixing of the longer conjugation length by the planar sidechains of MEH-PPV at room temperature.

In conclusion, we have studied the thermochromic effects in films of the light-emitting polymer MEH-PPV and two related copolymers. MEH-PPV films exhibited a striking color change from red to yellow when heated from room temperature to 100 °C. These films show promising thermochromic characteristics such as a rapid and reversible color change in a practical temperature range, without any observable phase or volume changes. We showed that heating results in a continuous blueshift and overall decrease in the polymer absorption and photoluminescence spectra that do not depend on crystallinity of polymer sidechains or on glass transition temperature. Both the HOMO and LUMO levels are shifting up with increased temperature at different rates to affect an overall increase in band gap energy. The demonstration of promising thermochromic properties in such a versatile, robust material opens up the possibility of realizing novel multifunctional device structures, and an understanding of how the energetic structure of such materials change with increasing temperature is crucial for future application development.

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