

Thermochromism of poly(phenylene) vinylene: untangling the role of polymer aggregate and chain conformation

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Scientific thrust area: Soft and biological nanomaterials

Research achievements:

Conjugated polymers with reversible thermochromic properties have potential applications toward smart windows, colorimetric sensors, and light emitting diodes.^{1,2} Thermochromic behavior for conjugated polymers has been reported for substituted polythiophenes, polyaniline, polydiacetylene and poly(phenylene vinylene) (PPV). For substituted polythiophenes, the thermochromism has been attributed to thermal vibrations imposing twisting of benzene rings resulting in a less coplanar polymer conformation¹. For MEH-PPV, thermochromic behavior has been related to conformational changes in the polymer chain leading to changes in the energetics of the HOMO and LUMO², and, alternatively, to enhanced solubility minimizing interchain interactions by untangling polymer aggregate into single polymer chains³.

We have investigated the temperature dependent photophysical properties of a conjugated polymer, poly{2,5-bis[3-(N,N-diethylammonium acetate)-1-oxapropyl]-1,4-phenylenevinylene} (DAAO-PPV, Figure 1a), in diluted solutions of toluene and 1,2-dichlorobenzene. We found DAAO-PPV to exhibit a reversible thermochromic behavior with color changes from red to green as the temperature raises from 278K to 373K (Fig.1b). This thermochromism is the result of untangling/formation of polymer aggregates due to varying solubility and conformational changes of single polymer chains within aggregate. By means of temperature-dependent UV-VIS spectroscopy, time-resolved fluorescence spectroscopy and dynamic light scattering spectroscopy we show how aggregation and polymer chain conformational changes manifest in the photophysics of DAAO-PPV. We find aggregates to dominate the spectroscopy of DAAO-PPVs at low temperatures, with absorption and emission bands peaking at red visible wavelengths. Time-resolved photoluminescence experiments demonstrate that within the aggregate, the energy is funneled from interchain excitons to single

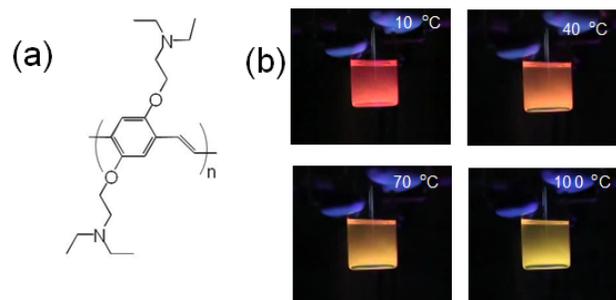


Figure 1. a). DAAO-PPV, b) temperature-induced color changes of DAAO-PPV diluted in toluene.

(or few) chromophoric sites, from which final luminescence occurs. By increasing the temperature, DAAO-PPV aggregates are driven into single polymer chains with absorption and emission bands peaking in the green visible wavelengths. The transition from polymer aggregate to single chain species involves an intermediate species, a loose aggregate whose size and conjugation length changes as a function of temperature due to weaker interchain interactions. By monitoring the hydrodynamic volume and the photophysics as a function of temperature

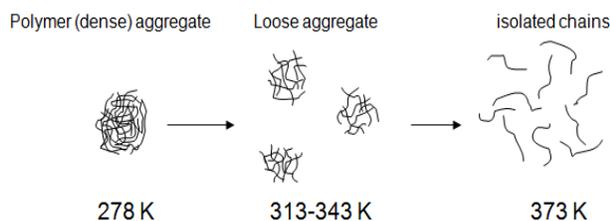


Figure 2. Model explaining thermochromism in DAAO-PPV: temperature increases polymer-solvent interactions untangling polymer aggregate into isolated chains via a loose aggregate state.

and solvent viscosity, we offer unequivocal evidence of how aggregates impact the optical and photophysical properties of the conjugated polymers. The model we propose to explain the thermochromism DAAO-PPV is shown in Figure 2. In this model, temperature untangles polymer aggregates into single chains by increasing polymer-solvent interactions, leading to solvent molecules to protrude inside the aggregate and to diminish interchain interactions. This makes the aggregate to swollen and to break apart in loose aggregates. Further increase in temperature leads to detachment of loose aggregates into isolated chains. Untangling of a dense aggregate into isolated chains seems to be a complex process, with no clear singular states at any of the temperatures points employed in this study. That is, over the temperature range investigated here, the sample is a blend of dense aggregate, loose aggregate and isolated chains with the temperature only biasing the contribution of each of these species.

Future work:

We are investigating the structure-optical properties in conjugated polymers, in particular the role of aggregate and chain conformation in defining the heterogenic optical properties of PPVs when dispersed in thin films. This particular study is addressed with time-resolved confocal fluorescence microscopy and it aims at understanding and controlling the heterogenic optical response of conjugated polymers for improved performance in devices such as organic solar cells or light emitting diodes.

Publications:

Chun-Chih Wang, Yuan Gao, Andrew P. Shreve, Hsing-Lin Wang* and Mircea Cotlet, "Thermochromism of poly(phenylene vinylene): untangling the roles of polymer aggregate and chain conformation", *, submitted to *J.Amer.Chem.Soc.*

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2. Leclerc, M., *Advanced Materials* **1999**, 11, (18), 1491-8.
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