Effect of residual monomer on the spectroscopic properties of polythiophenes

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The addition of some small molecules can red shift UV-Visible absorption and quench the fluorescence of poly(3-octadecylthiophene).

The electronic and spectroscopic properties of poly(3-alkylthiophene)s (PATs) have been intensely investigated over the last two decades.[1] The structure of PATs (regioregularity, molecular weight, and side chain) has been modified *via* novel synthetic methodology.[1–3] The variations have allowed the development of a strong understanding of the relationship between structure and spectroscopic properties in PATs.[4,5] Other research has focused on the influence of doping agents[6] and trace metal impurities[7] on the electronic properties. However, the effect of residual monomer on the spectroscopic and electronic properties of poly(3-alkylthiophene)s has received relatively little attention.

During the synthesis of low molecular weight poly(3-octadecylthiophene) (POT, M_n = 3,300, PDI = 2.5), we observed significant differences in the spectroscopic properties in the presence of residual 3-octadecylthiophene.†[2] Addition of 3-octadecylthiophene to POT results in a red shift of the optical absorption and reflection spectra (Fig. 1). The λ_{max} in absorption mode (a thin film on quartz) is shifted from 23040 cm^{-1} (434 nm) in the pure POT to 19960 cm^{-1} (501 nm) in a 1 : 1 w/w mixture of POT and monomer (a mole fraction of polymer X_p = 0.50). In reflection mode (a thin film on white paper) after conversion to Kubelka–Munck units of k/s, these maxima were 21140 cm^{-1} (473 nm) for X_p = 1.0 and 20550 cm^{-1} (487 nm) for X_p = 0.50. Stepwise addition of monomer to POT results in a gradual shift of optical reflection spectra (Fig. 2). The shift of the reflection spectra begins with mole fractions of monomer as low as X_m = 0.20 and is maximized at X_m = 0.50.

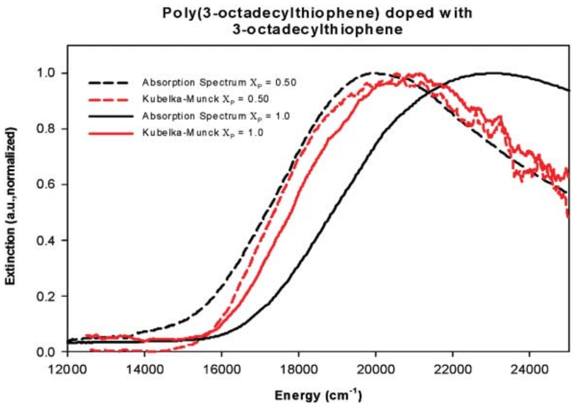

Fig. 1 Comparison of reflection spectra transformed into Kubelka–Munck space with transmission spectra (a film on quartz cuvette). All spectra are normalized.

UV irradiation of poly(3-octadecylthiophene) with and without 3-octadecylthiophene provides further insight into the altered spectroscopic properties. The addition of monomer results in a quenching of the fluorescence of the POT. Pure POT has a pink fluorescence that is easily detectable by optical inspection while the POT with added 3-octadecylthiophene (X_p = 0.50) has no observable fluorescence under UV irradiation (365 nm, Fig. 3). Decreases in fluorescence intensity and red-shifts of the optical

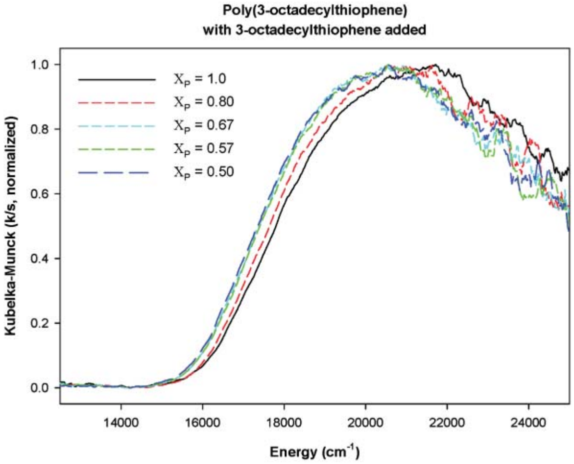

Fig. 2 Reflection spectra, transformed in Kubelka–Munck space and normalized, containing POT and 3-octylthiophene with the mole fraction (X_p) of POT varied from 1.0 to 0.5.

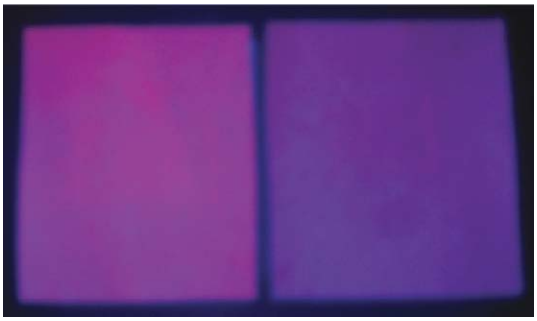

Fig. 3 Thin films of POT (left) and POT with 3-octadecylthiophene (right, X_p = 0.50) irradiated by UV light (365 nm).

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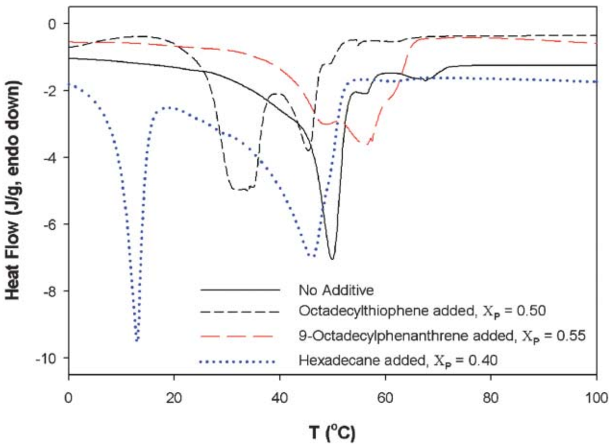

Fig. 4 DSC thermograms of POT and POT with additives.

absorption spectra in conjugated polymers and related small molecules have been attributed to improved π–π stacking.[8] The spectral changes occur due to delocalization of the wavefunction between adjacent π-stacked systems.

In order to develop an understanding of the source of the spectral shift of poly(3-octadecylthiophene) with added 3-octadecylthiophene, the structure of small molecule additives was varied. The trends suggest that the shifts of the optical absorption spectra have a complex relationship. The spectral shift occurs only with additives containing a long straight chain alkane with length comparable to the octadecyl substituent of the polymer and a thiophene, benzene, or bromide end group. Comparable spectral shifts are observed upon the addition of 1-bromooctadecane, 1-bromohexadecane, octadecylbenzene, 3-dodecylthiophene, and 3-octadecylthiophene. However, the presence of short straight chain dibromides (1,10-dibromodecane), mixtures of alkanes (mineral oil), linear alkanes (hexadecane), or longer chain alkyl halides (1-bromotetracosane) does not result in a change in the optical absorption spectrum. A spectral shift is also not observed when the additive contains a large aromatic end group such as 9-octadecylphenanthrene. Interestingly, the additives appear to have an effect comparable to 3-octadecylthiophene or no effect. None of the additives has an intermediate effect on the spectra.

Fig. 4 shows the DSC thermograms of POT and several mixtures. The pure polymer has a prominent endotherm at 49.9 °C, attributed to melting of the alkyl side chains. Upon mixture with the monomer (X_p = 0.50), two features are present, endotherms at 34.2 and 45.4 °C. These two peaks are assigned to monomer melting (depressed from the melting point of the pure monomer, 41 °C) and the polymer side chain melting, depressed by the impurity. Similar effects are observed with 9-octadecylphenanthrene (endotherms at 48.8 and 56.2 °C, respectively assigned to polymer side chain melting and 9-octadecylphenanthrene melting, depressed from the pure melting point of 79 °C). Finally, addition of hexadecane to POT shows two prominent endotherms at 13.0 °C (assigned to hexadecane melting) and 46.1 °C (assigned to alkyl side chain melting in POT). All of the additives cause depression of the side chain melting in POT, indicating that each of the additives solvates the octadecyl group. However, note that neither 9-octadecylphenanthrene nor hexadecane causes a spectroscopic shift.

Spectral changes of POTs are clearly related to the structure of the additive. The additives likely integrate into the ordered structure of poly(3-octadecylthiophene)s, allowing the polymer to form more highly ordered polythiophene aggregates.[9] The effect does not appear to be a simple solvation phenomenon since some additives that provide a melting point depression to the poly(3-octadecylthiophene), such as hexadecane, do not alter the spectroscopic properties. The additives must be able to "solvate" the long alkyl side chains *and* integrate into the π-stacking. The improved π-stacking is responsible for the shift of absorption maxima and fluorescence quenching. The results suggest that the presence of residual monomer or other small molecule impurities can have a significant impact on the spectroscopic or electronic properties of conjugated polymers.

Notes and references

† **Poly(3-octadecylthiophene)**. Under a positive atmosphere of nitrogen, 2,5-dibromo-3-octadecylthiophene (31.2 g, 63.2 mmol) was dissolved in 320 mL of THF. Methylmagnesium bromide (54 mL, 1.4 M solution in toluene/tetrahydrofuran 75/25) was added and the solution was heated to reflux, followed by addition of Ni(dppp)Cl_2 (3.4 g, 6.3 mmol). The reaction mixture was stirred for 30 min. The polymer was precipitated in 1000 mL methanol and purified *via* Soxhlet extraction with methanol to afford POT (15.0 g, 71%).

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