

Enhanced photo and thermal oxidative stability of the charge-transfer complexes of a conjugated polymer

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To clarify degradation mechanisms of the charge-transfer complexes of poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) with organic acceptors [*e.g.*, trinitrofluorenone (TNF)], the corresponding MEH-PPV/TNF blends have been studied by various methods.

The thermal oxidative stability of a conjugated polymer (CP) is very important for its processing and exploitation, while the photo- and/or thermo-oxidation of polymers is a major factor that leads to shortening the lifetime and lowering the efficiency of various devices based on them.^{1,2} Therefore, the elucidation of mechanisms of such a degradation and correct service life predictions are necessary for optimising CP-based devices.

Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) is now a 'classic' model for tackling generic problems of CPs.³ It has been reported recently⁴ that MEH-PPV is capable of forming intermolecular charge-transfer complexes (CTCs) with small organic acceptors such as 2,4,7-trinitrofluorene-9-one (TNF).

The drop-cast films of both pristine MEH-PPV (Sigma-Aldrich, MW = 125000) and MEH-PPV blends with TNF (Aldrich, mp 171, > 98% purity) were prepared from chlorobenzene by varying the polymer concentration in the range 0.5–2 g dm⁻³ and the TNF:MEH-PPV molar ratio in the range 0.01–1.

The susceptibility of neat MEH-PPV to photo oxidation and a comparison with that of MEH-PPV/TNF blends is illustrated in Figure 1. An immediate blue shift of λ_{\max} and a progressive reduction of A_{\max} were observed in the course of irradiation; this was explained by shortening the π -electron delocalization length of the polymer. The FTIR spectra of the same films measured before and after irradiation exhibited new bands at 1279 and 1691 cm⁻¹ unambiguously indicating⁵ the photo oxidation of PPV. It is evident that MEH-PPV/TNF blends exhibit

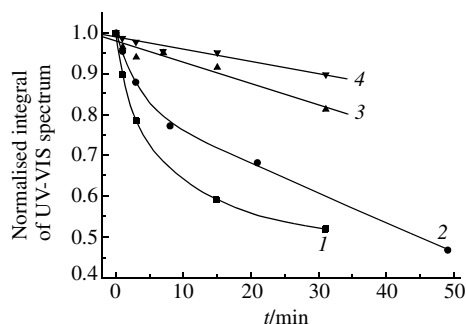


Figure 1 The integral UV-VIS absorption vs. irradiation time; (1) neat MEH-PPV, (2) MEH-PPV:TNF, 1:0.3; (3) MEH-PPV:TNF, 1:0.6; (4) MEH-PPV:TNF, 1:1.

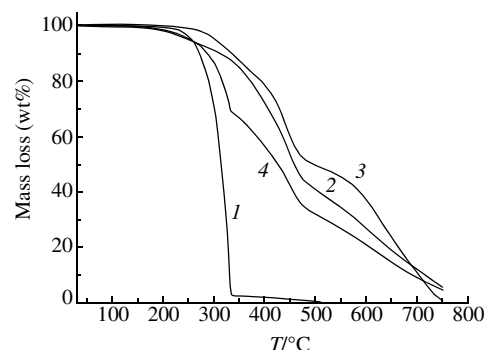


Figure 2 Experimental TGA curves for (1) neat TNF, (2) neat MEH-PPV, (3) MEH-PPV:TNF, 1:0.2 and (4) calculated TGA curve built by simple addition of the components partial contributions for the same MEH-PPV/TNF blend.

a markedly improved photo-oxidative stability as compared to that of the neat polymer.

Moreover, for TNF contents increasing in the range 5–25 mol%, the blends demonstrated a clear systematic gain in their thermal-oxidative stability. It is of importance that both of the blend components have revealed a synergistic behaviour in terms of the stability enhancement (Figure 2). Comparative experiments have shown that fullerene C₆₀ is also capable of stabilizing MEH-PPV, but in much higher concentrations.

Experimental data obtained by other methods indicate spectacular non-covalent interactions between the donor and the acceptor within the same (5–25 mol%) range of TNF contents. Partial electron density transfer from the MEH-PPV polymer onto TNF molecules involved in the corresponding CTC (according to FTIR and Raman data) should, in principle, reduce the susceptibility of the polymer to oxygen. It is likely that the quenching of the triplet states excited on the macromolecules can effectively prevent triplet–triplet annihilation reactions, which are normally feasible in the presence of reactive singlet oxygen.⁶

The kinetic studies of both MEH-PPV/TNF blends and the pristine polymer (using a model-free Friedman analysis, non-linear regression analysis of the kinetic parameters,⁷ and lifetime prediction) has indicated that four-step thermal-oxidative degradation processes are operative in the system. The experimental results suggest that the complexed TNF (or the corresponding TNF/MEH-PPV charge-transfer complex) is capable

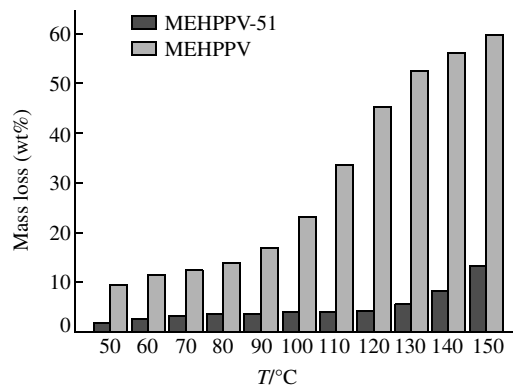


Figure 3 Comparison of one year predicted life-time behaviours for the neat MEH-PPV and MEH-PPV/TNF (1:0.2) blend in ambient (air) atmosphere.

of effectively intercepting radical species that could trigger thermal oxidation processes in the system. This study also demonstrated the stabilizing effect of the acceptor in the blends: the lifetimes predicted for MEH-PPV/TNF blends at practically important temperatures (60–100 °C) are higher than those of the neat conjugated polymer by three orders of magnitude (Figure 3).

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