Competition Between Polaronic and Bipolaronic Charge States in the Oxidative and Protonic Doping of Model Oligomers of Poly(dialkoxyphenylene vinylene)

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Quantitative ESR measurements on oxidatively and protonically doped model oligomers of poly(dialkoxyphenylene vinylene) indicate that bipolaronic charge states dominate both doping processes.

The mechanism of charge state generation in electroactive polymers continues to be an area of intense interest. Although, it is generally regarded that bipolarons are the dominant charge carriers in conjugated pi-electron polymers having non-degenerate ground states, such as polythiophene and poly(p-phenylene vinylene),[1] Han and Elsenbaumer have reported that non-oxidative protonic doping (CF_3CO_2H) of poly(dibutoxyphenylene vinylene) (PDBPV) is dominated by polaron-like charge states resulting from ring protonation and subsequent internal redox of an initially formed bipolaron.[2]
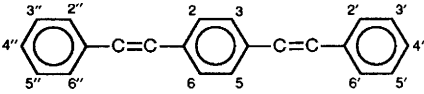
In a continuing study of charge state generation in model compounds,[3,4] we have previously investigated the comparison between oxidative ($SbCl_5$) and protonic doping of substituted diphenylpolyenes and reported that the optical spectra obtained in both cases were more consistent with stable bipolaron formation.[5] Preliminary ESR measurements were in agreement with this interpretation.[5,6] We can now report that quantitative ESR measurements followed as a function of time on a series of model oligomers of poly-(dimethoxyphenylene vinylene) (PDMPV) and PDBPV confirm our original postulate that bipolaron-like charge states are preferentially formed in protonic as well as oxidative doping techniques.

Oligomers of alkoxy-substituted PPV (dimer and trimer) were prepared by Wittig methodology.[7,8] Solutions of these oligomers (10^{-5} mol dm^{-3} in CH_2Cl_2) were oxidatively doped with an excess of $SbCl_5$ and the ESR response monitored over a 24 h period. Protonic doping was accomplished by preparing 10^{-4} mol dm^{-3} solutions of the oligomers in neat CF_3CO_2H,

and the ESR response monitored in a similar fashion. As we have previously noted,[5,6] protonic doping is a relatively slow process compared to $SbCl_5$ oxidation. ESR spectra were recorded with an IBM-Bruker ER 200D at room temperature upon mixing, at 2 and 24 h intervals for comparison purposes.

Han and Elsenbaumer based their assignment of polaronic charge state dominance in PDMPV and PDBPV doped solutions on the observation of three prominent absorption bands (0.6, 0.8 and 1.54 eV) and a strong ESR signal with a g value of 2.0019 with a ΔH_{pp} of 6.9 G (1 G = 10^{-4} T), however, no estimate was made of the concentration of charge carrier with respect to the number of repeat units. The results from the oxidative and protonic doping of our model PPV oligomers are shown in Table 1. As can be readily seen, in no case does the percentage of polaronic species approach that of the doped species. In fact, the concentration of polaron-like species is at a maximum immediately upon mixing for $SbCl_5$-doping, in accord with our previous VIS–NIR optical studies,[3,6] and declines to less than 1% of the total charge species concentration. The results are similar in the protonically doped species. After 24 h, the polaron concentration is remarkably similar for both doping techniques.

We conclude from the above data that both protonic and oxidative doping of PPV oligomers yield bipolaronic (BP) states predominantly, and that polymer ESR activity is no guarantee that polaronic (P) charge states dominate active charge carriers. For both oxidative and protonic doping we prefer a model in which P and BP states are in equilibrium in solution, with spinless BP states dominating. This can be represented

Table 1 ESR spectra of doped substituted PPV oligomers

Substituents	Spin concentration/mol dm^{-3}				
	SbCl$_5$/CH$_2$Cl$_2$^{a}			CF$_3$CO$_2$H^{a,b}	
	0 h	2 h	24 h	2 h	24 h
2,5,4',4"(OMe)$_4$	3×10^{-6}	1×10^{-7}	9×10^{-7}	3×10^{-6}	1×10^{-6}
2,5(OMe)$_2$,4',4"(OC$_8$H$_{17}$)	8×10^{-6}	3×10^{-7}	7×10^{-9}	7×10^{-6}	1×10^{-6}
2,5,2',5',2",5"(OMe)$_6$	8×10^{-6}	3×10^{-6}	5×10^{-7}	3×10^{-6}	2×10^{-7}
2,5,2',5',2",5"(OBu)$_6$	1×10^{-5}	3×10^{-6}	8×10^{-7}	4×10^{-6}	9×10^{-7}
PDBPV-trimer	1×10^{-5}	5×10^{-6}	1×10^{-6}	1×10^{-6}	—

^{a} Initial polyene concentration 10^{-4} mol dm^{-3}. ^{b} ESR signal at mixing too low to measure due to slow nature of CF$_3$CO$_2$H doping.

schematically as follows, where N represents the undoped oligomer or polymer: (*a*) Oxidative Doping: N $\xrightarrow{-e}$ P $\xrightarrow{-e}$ BP; (*b*) N $\xrightarrow{2H^+}$ BP $\xrightleftharpoons{N}$ P$_1$ + P$_2$. Therefore, even when a small percentage of P states persist, the bipolaron will dominate the absorption spectra. Mesomeric substituent effects will of course influence the relative position of the P–BP equilibrium.

It has recently been pointed out by DeMelo and Silbey[9–11] theoretically and Cao, *et al.*[12] experimentally, that non-linear optical response can be significantly enhanced by polaronic or biopolaronic charge states. We are currently investigating the consequences of our results on the non-linear optical properties of oxidatively or protonically doped electroactive oligomers, which will hopefully result in new design criteria for third order NLO materials.[13]

Received, 6th September 1991; Com. 1/04665I

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