

# Polaron and bipolaron formation in model oligomeric extended $\pi$ -electron systems: Studies towards the rational design of electroactive polymers for non-linear optics applications

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(Received 15 September 1988; revised 1 December 1988; accepted 13 December 1988)

Oligomers related to poly(*p*-phenylene vinylene) and poly(2,5-thienylene vinylene) can be oxidatively doped with  $\text{SbCl}_5$  in  $\text{CH}_2\text{Cl}_2$  solution, and successive polaron and bipolaron formation can be followed by absorption spectroscopy. Electron-donating groups, such as  $\text{CH}_3\text{O}$ -, stabilize bipolaron states for several hours at room temperature in contact with moist air, which indicates that highly delocalized oligomeric systems may be useful for modelling approaches to enhancing non-linear optical properties in electroactive polymers in which the size of the delocalized domain plays an important role.

(Keywords: poly(*p*-phenylene vinylene) oligomers; poly(2,5-thienylene vinylene) oligomers; electroactivity; non-linear optics; electron delocalization; polaron; bipolaron)

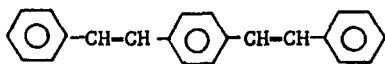
## INTRODUCTION

Electroactive polymers have been of considerable interest over the past decade due to the novel metallic conductivity achieved upon either chemical or electrochemical doping<sup>1</sup>. The nature of charge delocalization or storage has also attracted a great deal of attention, and the basic chemistry and physics of soliton, polaron and bipolaron generation and propagation have been studied extensively<sup>2</sup>. Recently, large non-linear optical effects have been observed in polyacetylene and heteroaromatic polymers and third-order effects have been related to the extent of electron delocalization<sup>3</sup>. The present work is an attempt to see if polaronic or bipolaronic states can be stabilized by polar substituent groups in oligomeric systems which model some well characterized electroactive polymers. Such stabilization may indeed suggest how new polymer systems can be designed to maximize non-linear optical (NLO) properties.

## EXPERIMENTAL

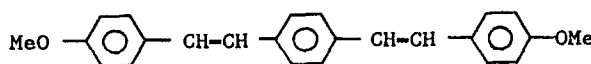
### Preparation of samples

All of the compounds reported were prepared by standard Wittig condensation using tributylphosphonium salts and the corresponding aromatic or heteroaromatic dialdehydes in either dimethylformamide (DMF) or ethanol (EtOH) solution, and utilizing sodium ethanoate ( $\text{NaOEt}$ ) as the base.

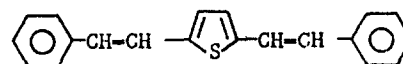


Compound I was obtained from benzyltributyl-

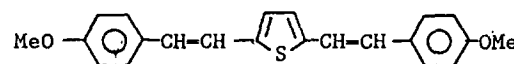
phosphonium bromide and terephthalaldehyde (67%, recrystallized from DMF; m.p.  $262^\circ\text{C}$  (lit.<sup>4</sup>  $258^\circ\text{C}$ )).



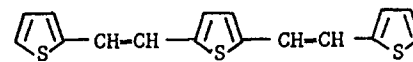
Compound II was obtained from 4-methoxybenzyltributylphosphonium bromide and terephthalaldehyde (64%, recrystallized from DMF; m.p.  $303-7^\circ\text{C}$  (lit.<sup>5</sup>  $307-8^\circ\text{C}$ )).



Compound III was obtained from benzyltributylphosphonium bromide and thiophene-2,5-dicarboxaldehyde (80%, recrystallized from toluene/DMF; m.p.  $189-91^\circ\text{C}$ ).

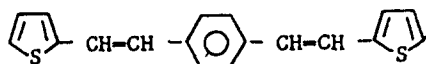


Compound IV was obtained from 4-methoxybenzyltributylphosphonium bromide and thiophene-2,5-dicarboxaldehyde (27%, recrystallized from toluene/DMF; m.p.  $241-2^\circ\text{C}$ ).



Compound V was obtained from thiophene-2-methyltributylphosphonium bromide and thiophene-2,5-dicarboxaldehyde (35%, recrystallized from toluene/DMF; m.p.  $130-2^\circ\text{C}$ ).

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Finally, compound VI was obtained from thiophene-2-methyltributylphosphonium bromide and terephthaldehyde (46%, recrystallized from toluene/DMF; m.p. 264–5°C).

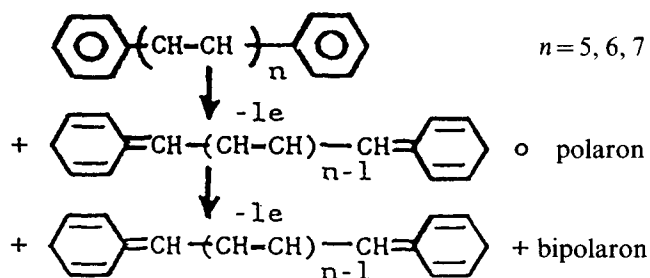
All compounds had satisfactory elemental analyses, and yields are for purified recrystallized products.

#### Doping procedure

Solutions of compounds I–VI in  $\text{CH}_2\text{Cl}_2$  ( $10^{-5}$  M) were prepared and the u.v./vis. spectra recorded. Excess  $\text{SbCl}_5$  was added as a  $10^{-3}$  M solution in  $\text{CH}_2\text{Cl}_2$  and the resulting spectrum recorded after 1 min\*. In most cases both polaron and bipolaron bands could be discerned. The solution was then allowed to stand in contact with air for various times. In all cases complete conversion to the bipolaron state had occurred after 1 h and the spectrum recorded. These results are shown in Figures 1–6.

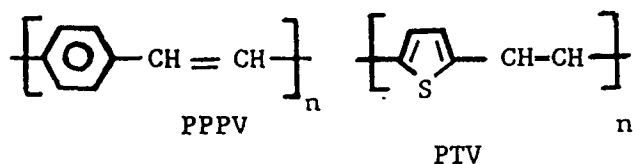
## RESULTS AND DISCUSSION

Several electroactive polymer systems have been studied over the past several years in which successive polaron and bipolaron formation has been observed. In order to determine whether this formation could be modelled by small oligomeric structures, a series of  $\alpha,\omega$ -diphenylpolyenes were doped with  $\text{FeCl}_3$  and  $\text{SbCl}_5$  in dilute solution recently by Spangler and coworkers, and the rapid spectroscopic changes interpreted on the basis of successive polaron and bipolaron formation<sup>6</sup>. Substitution of polar substituents



in the *para* positions of the terminal phenyl groups greatly increases the stability of the bipolaron state by mesomeric interaction, and also significantly reduces the oxidation band gap<sup>7</sup>.

One polymer system that is closely related to the above diphenylpolyene series, and has also shown significant oxidative electroactivity, is poly(*p*-phenylene vinylene) (PPPV). A heteroaromatic counterpart is poly(2,5-thienylene vinylene) (PTV)<sup>8,9</sup>.



U.v./vis. absorption photoluminescence and photo-induced absorption studies of PPPV have allowed

\* A 2-fold to 10-fold excess is sufficient to observe rapid polaron and bipolaron formation on the timescale reported in this work, although the concentration of excess reagent does not appear to be critical

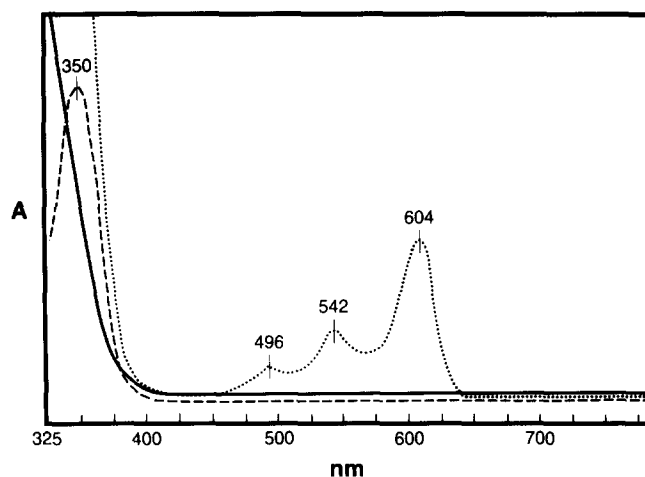


Figure 1 Oxidative doping of I with excess  $\text{SbCl}_5$ : initial polyene (---); 1 min after doping (.....); 15 min after doping (—)

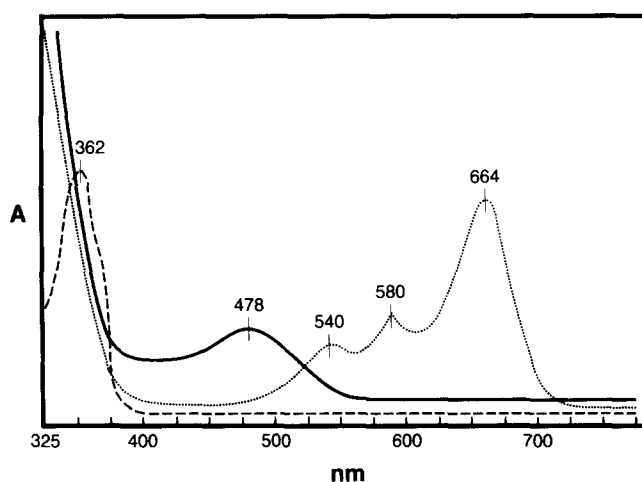


Figure 2 Oxidative doping of II with excess  $\text{SbCl}_5$ : initial polyene (---); 1 h, after doping (—)

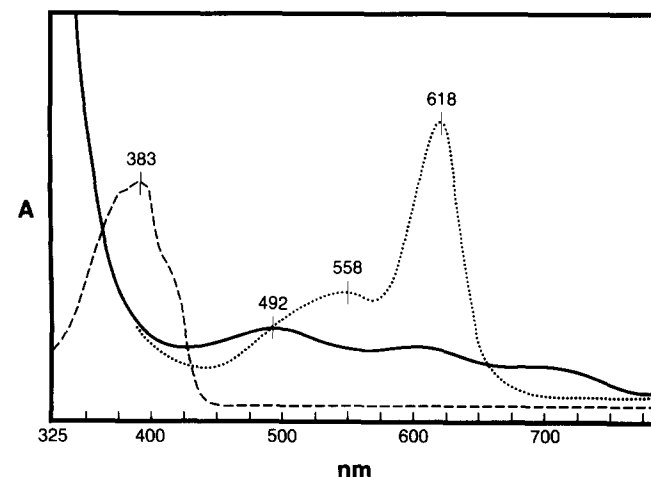


Figure 3 Oxidative doping of III with excess  $\text{SbCl}_5$ : initial polyene (---); 1 min after doping (.....); 30 min after doping (—)

estimates of the polaron and bipolaron energy levels,  $\pi-\pi^*$  transitions for the various conjugated oligomeric segments of the stretch-oriented polymer film and the number of conjugated segments giving rise to electron delocalization<sup>10</sup>. However, with those samples the problem remains of the inhomogeneous distribution of

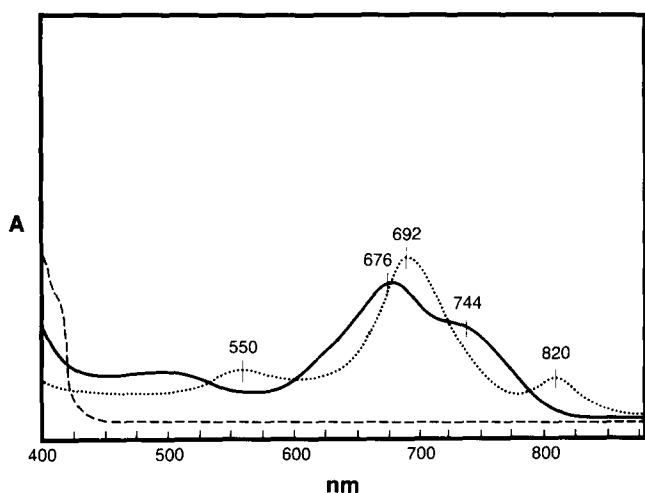


Figure 4 Oxidative doping of IV with excess  $\text{SbCl}_5$ : initial polyene (----); 1 min after doping (.....); 1 h after doping (—)

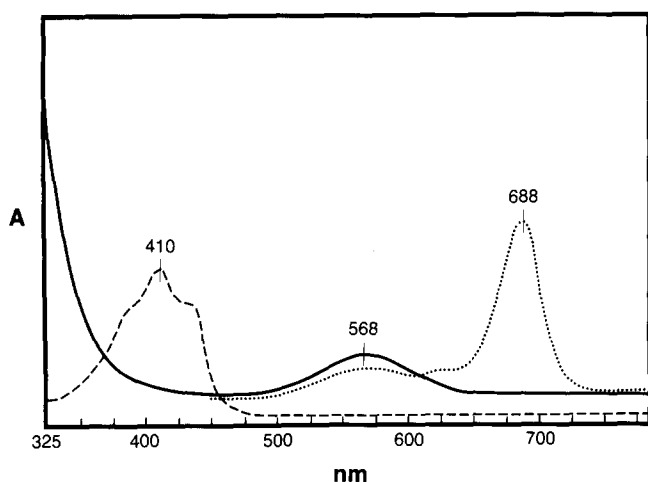


Figure 5 Oxidative doping of V with excess  $\text{SbCl}_5$ : initial polyene (----); 1 min after doping (.....); 15 min after doping (—)

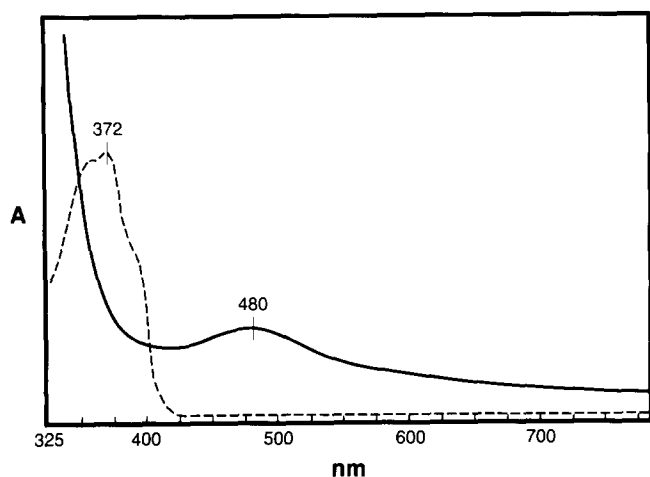
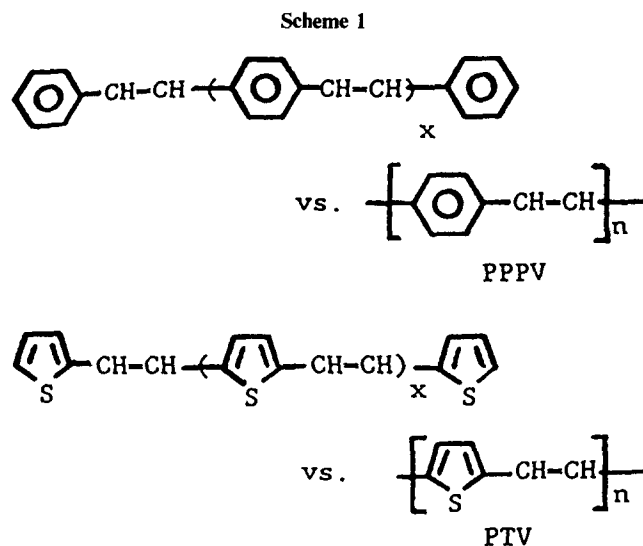


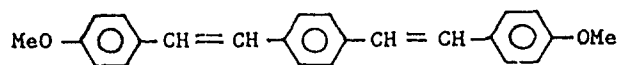
Figure 6 Oxidative doping of VI with excess  $\text{SbCl}_5$ : initial polyene (----); 15 min after doping (—)

conjugated segments, and thus, upon doping, a range of delocalization lengths are obtained. In the bulk material the number range and distribution of these charged domains is difficult to estimate, and an average value is often used to explain physical and spectroscopic properties.

We have therefore proposed that oligomeric model compounds may be useful in examining how delocalized domains can be formed and stabilized in order to design NLO active polymers (see Scheme 1).



Substitution of methoxy groups on the terminal rings thus may facilitate delocalization over a specific number of atoms and allow a direct comparison between delocalization length, polaron (P) and bipolaron (BP) energy levels and the optical band gap.



Solutions of compounds I–VI were oxidatively doped in  $\text{CH}_2\text{Cl}_2$  solution and the results are shown in Figures 1–6, and the absorption characteristics summarized in Table 1.

In general, the molar absorptivities of P and BP bands are much weaker when a quinoidal unit is required for charge delocalization. The 2,5-thienylene unit is a much more efficient charge transmitter. This would imply that thiophene units in the oligomer or polymer interior (as opposed to end-caps) would be preferable for charge delocalization. Thus, since PPPV and PTV have similar bulk conductivities via interchain electron hopping, conductivity may not be a good predictor for third-order non-linear activity. In fact, the two properties may be only incidentally correlated by having similar molecular charge states, and design considerations for maximizing either electrical conductivity or NLO activity may in fact be unrelated. The added stabilization obtained by mesomeric delocalization interaction with polar substituent groups is clearly demonstrated by comparing I

Table 1 Oxidative doping of PPPV and PTV oligomers

Compound	$\pi$ - $\pi^*$ transition (nm)	P transition (nm)	BP transition (nm)
I	350	604, 542, 496	Not observed
II	362	664, 580, 540	478
III	383	618, 558	492
IV	396	820 (692)	744, 676
V	410	688	568
VI	372, 366	Not observed	480

and II, and particularly III and IV where the effect is pronounced on both P and BP states. DeMelo and Silbey<sup>11</sup> have most recently considered the relationship problem of conjugation in polyenes, solitons, polarons and bipolarons to non-linear polarizabilities. They have suggested that polar substituents may yield materials of high non-linear hyperpolarizabilities. We have now demonstrated that these groups enhance delocalization stability. Since theoretical calculations<sup>12</sup> suggest that bulk  $\chi^{(3)}$  should be related to the sixth power of the electron delocalization length, it can further be argued that in order to obtain polymers with large third-order NLO activity, the design aspect should concentrate on extending the solitonic, polaronic or bipolaronic domains, and their concentration. We have shown now that this could be achieved by judicious substitution of mesomerically active polar groups.

## CONCLUSIONS

In summary we believe the results give us a firm foundation from which we can explore whether extending the  $\pi$ -system to longer oligomeric lengths or stabilizing the delocalization by mesomeric interaction are of similar or complementary importance. Accumulation and understanding of such relationships will eventually allow the rational design of oligomers or polymers with specific NLO characteristics.

## ACKNOWLEDGEMENTS

The authors would like to thank Professor Larry Dalton for many helpful discussions during the course of this

work and partial support of one of the coauthors (TH) by Hoechst-Celanese Corporation.

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