# Oxidative Doping of Intermediate Length Polyenes: Attempted Oligomeric Modelling of Doped Polyethyne

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Polyenes containing 7, 8, 9, and 10 conjugated double bonds form stabilized bipolarons upon oxidative doping with antimony pentachloride, whose spectra may be useful in modelling optical changes which occur during the polyethyne doping process.

The chemistry of polyethyne (PE) and other electro-active materials has been an area of intense interest since the discovery that metallic conductivity could be attained by simple chemical or electrochemical oxidation (doping).[1] An integral and important aspect of the study of bulk charge transport in PE is the identification of the relative importance of solitons, polarons, and bipolarons at various stages of the doping process.[2] It is now generally recognized that these charged states exist in finite localized domains in the vicinity of the oppositely charged counterion, and Kamiya and Tanaka[3] have recently postulated that soliton and/or polaron domains of 15—20 C-atoms alternate with undisturbed PE domains in the early stages of PE doping. Most recently, it has been found that delocalized electroactive polymers, such as PE and polythiophene, have significant non-linear optical (NLO) activity, and that, in particular, third order NLO effects can be related to the extent of this delocalization.[4] Dalton has suggested that electron delocalization giving rise to significant $\chi^3$ activity may in fact be independent of polymer or oligomer type. We now report that the bipolaric states can indeed be induced in PE-type oligomers with delocalization lengths of from 14 to 20 C-atoms.

We have recently reported[5] a general method for the preparation of symmetrically substituted polyenes containing either an odd or even number of double bonds (Scheme 1). We had also previously reported a preliminary account of the preparation of $Me(CH{=}CH)_nMe$ ($n = 7$ and 8) as well as their doping behaviour in solution with iodine.[6] We have now

**Table 1.** Synthesis and electronic absorption characteristics of $Me(CH{=}CH)_nMe$.

| | Precursor | | Solvent; | % | |
|---|---|---|---|---|---|
| $n$ | $x$ | $y$ | $t$/°C | Yield | $\lambda_{max.}$/nm ($\log a_{max.}$)[a] |
| 7 | 2 | 2 | EtOH; 0 | 70 | 398(4.72), 375(4.75), 355(4.53) |
| 8 | 2 | 3 | DMF; 0 | 40 | 420(4.73), 395(4.75), 375(4.56) |
| 9 | 3 | 2 | DMF; 50 | 37 | 443(4.77), 416(4.80), 393(4.64) |
| 10 | 3 | 3 | DMF; 50 | 33 | 460(4.60), 431(4.78), 406(4.56) |

[a] $CH_2Cl_2$ Solution, peak shoulders not included.

$$2\,R(CH{=}CH)_xCHO + Bu_3\overset{+}{P}CH_2(CH{=}CH)_yCH_2\overset{+}{P}Bu_3,\ 2Br^- \xrightarrow{\text{Base/solvent/50—100 °C}} R(CH{=}CH)_z \qquad z = 2x + y$$

**Scheme 1.** Base: NaOMe or KOBu$^t$; solvent = EtOH or dimethylformamide (DMF); R = Ph or Me.

improved these preparations and extended the series to $n = 9$ and 10. These polyenes are formed in the all-*E*-configuration and are extremely air-sensitive whether in solid form or in solution. Even storage at −40 °C under inert atmosphere only partially retards the irreversible polymerization process over extended periods of time. The polyenes can be handled at room temperature under an inert atmosphere or in $CH_2Cl_2$ solution for several hours without any significant decomposition or polymerization. The u.v. absorption characteristics of these polyenes are outlined in Table 1.

Our previous studies[7] of the oxidative doping of α,ω-diphenyl polyenes were interpreted on the basis of successive one electron transfers yielding polaron and bipolaron states. The polaron state is formed first as indicated by e.s.r. spectroscopy, but is then rapidly converted to the more stable bipolaron state [reaction (1)]. When dilute solutions ($CH_2Cl_2$) of $Me(CH{=}CH)_nMe$ are oxidized with excess of $SbCl_5$, an almost instantaneous optical bleaching of the original polyene spectrum occurs with the simultaneous formation of a new absorption band at much lower energy, analogous to the population of mid-gap states in the oxidative doping of PE. The position of the band shifts continuously to lower energy with increasing conjugation length. In contrast to the diphenylpolyene series there is no spectral evidence for the intermediary polaron state; however, the bipolarons may be stabilized for several hours at 0 °C under an inert atmosphere. The spectral characteristics of oxidized species are shown in Table 2. It should be emphasized that the initial extinctions of the bipolaron bands are all greater than for the original polyenes.

$$R(CH{=}CH)_nR \xrightarrow{-1e} \underset{\text{polaron}}{R\overset{+}{C}H(CH{=}CH)_{n-1}\overset{\bullet}{C}HR} \xrightarrow{-1e} \underset{\text{bipolaron}}{R\overset{+}{C}H(CH{=}CH)_{n-1}\overset{+}{C}HR} \qquad (1)$$

For $n = 10$, the bipolaron is delocalized over 20 C atoms approximating the lightly doped state of polyethyne. The most surprising feature of this study is our inability to observe the polaron state spectroscopically, particularly since polarons are regarded as being of major importance in doped PE and can easily be observed in the diphenylpolyene series. The successful generation of relatively highly delocalized charged states in simple polyene oligomers may have important implications, not only from the viewpoint of qualitatively describing electroactivity in extended π-systems, but also in designing oligomers or polymers for non-linear optics applications if electron delocalization effects indeed prove to be the dominant aspect of greatly enhanced third-order hyperpolarizabilities.

**Table 2.** Electronic absorption spectra for polyene bipolarons.

| $Me(CH{=}CH)_nMe$ | $\lambda_{max.}$/nm[a] | eV (max. absorption) |
|---|---|---|
| $n = 7$ | 690, *646*, 606 | 1.91 |
| 8 | *716*, 668 | 1.73 |
| 9 | *781*, 726 | 1.58 |
| 10 | *821*, 794 | 1.50 |

[a] Peaks of maximum extinction in italics.

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