Oxidative doping of polyenes derived from chemically dehydrochlorinated poly(vinyl chloride)

Eryl D. Owen* **and Mishgan M. Al-Awar**
School of Chemistry and Applied Chemistry, University of Wales College of Cardiff,
PO Box 912, Cardiff CF1 3TB, UK

(Received 18 March 1993; revised 7 October 1993)

Polyene sequences produced by chemical dehydrochlorination of poly(vinyl chloride) react with antimony pentachloride to form species with strong absorptions in the visible and near-infra-red regions of the spectrum, the detailed positions and relative intensities of which depend on the [polyene]/[$SbCl_5$] ratio. The absorbances are discussed and compared with those described for related systems.

(Keywords: polyenes; poly(vinyl chloride); oxidative doping)

INTRODUCTION

The structure and reactivity of polymers containing highly delocalized π-electron sequences have been areas of continuing interest for more than a decade. Attention was originally centred on the remarkable increases in electrical conductivity that were produced as the polymers were chemically or electrochemically 'doped', in some cases attaining values in the metallic regime. More recently, it has become apparent that the non-linear optical properties of these polyene systems may be at least as important and exploitable a characteristic.

The details of the extent and nature of the charge delocalization, as well as the interrelations at various stages of the process between the soliton, polaron and bipolaron states, which have been postulated as charge carriers, have been intensively studied but are far from being completely understood. In many cases, the intractable nature of the materials, as well as their environmental sensitivity, have proved to be handicaps as far as characterization and commercial exploitation are concerned.

Spangler[1] and others have synthesized and studied a variety of relatively low-molecular-weight model systems containing up to six double bonds and described the polaronic (radical cation) and bipolaronic (dication) states formed upon interaction with strong oxidizing agents such as antimony pentachloride, $SbCl_5$. Their work has revealed several interesting and unexpected features, including, for example, substantial differences between band-gap values and ease of charge stabilization for phenyl and thienyl end-groups, which suggest that useful optical absorptions may be optimized by careful control of end-group structures[2]. They have also pointed to possible advantages of systems in which electroactive units are alternated with inactive segments.

As part of our long-standing interest in the reactivity of polyene sequences formed by dehydrochlorination of poly(vinyl chloride) (PVC)[3,4], we have investigated the reactions of these polyenes with a number of metal halide systems, including $SbCl_5$. We present here a preliminary account of some strongly absorbing species that are formed, which bear strong resemblances to those described in other systems[5] and which may be amenable to the production of stable optical products.

EXPERIMENTAL

Suspension PVC (supplied by European Vinyl Corporation International) was degraded chemically for 2 h using the method described by Shindo[6], and is referred to as CPVC-2. The material was thoroughly washed to remove excess NaOH, dried and stored in a desiccator. Solutions were prepared by stirring a quantity of the material in dichloromethane (DCM) for 1 h at ice temperature and then filtered. They were combined with DCM solutions of $SbCl_5$ under standard dry-box conditions.

Tetrahydrofuran (THF) and dichloromethane were dried by the standard methods described previously[3,4].

RESULTS

PVC, which had been chemically degraded for 2 h (CPVC-2), was dissolved in DCM, and 5 cm^3 of the solution was added to a DCM solution (0.05 cm^3) of $SbCl_5$ (0.1 M). The resulting solution was deep blue and the visible absorption spectrum showed strong absorptions over the 500–800 nm region, with pronounced maxima at 590 and 650 nm and a shoulder around 720 nm (*Figure 1a*). At the same time, the characteristic absorption of the degraded PVC (polyenes) (*Figure 1b*) decreased markedly. When the experiment was repeated using a higher initial quantity of $SbCl_5$ (0.5 cm^3 of a 0.1 M solution), the positions of the absorptions in the 500–800 nm region remained essentially unchanged but were accompanied by strong new absorptions at higher energy (400–550 nm), with a pronounced, broad maximum around 446 nm (*Figure 1c*).

When DCM solutions containing a higher initial

---

*To whom correspondence should be addressed

0032-3861/94/13/2840–04

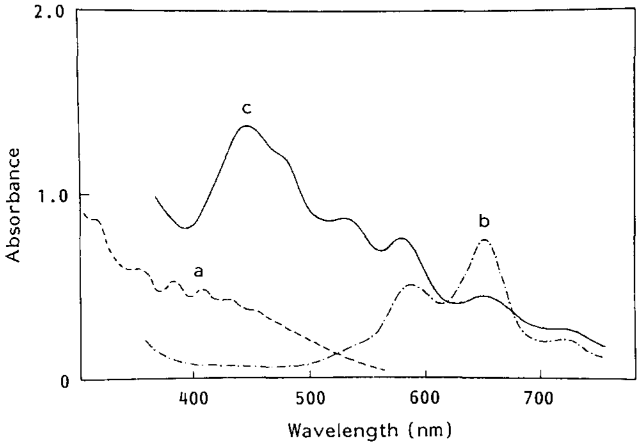


Figure 1 Absorption spectra: (a) DCM solution of CPVC-2 (see text); (b) solution (a) with added (10^{-4} M) $SbCl_5$; (c) solution (a) with added (10^{-3} M) $SbCl_5$

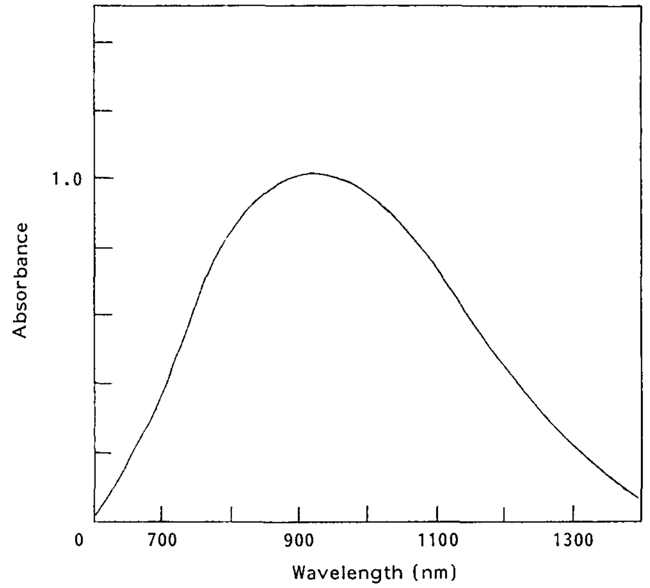


Figure 2 Absorption spectrum of a DCM solution of CPVC-2 (see text) with added (2×10^{-5} M) $SbCl_5$ in the near-infra-red region

concentration of polyenes were combined with a lower concentration of $SbCl_5$ (2×10^{-5} M), producing a lower dopant/polyene ratio, an absorption developed immediately that had a maximum intensity around 950 nm and extended well into the near-infra-red region (*Figure 2*). The corresponding decrease in intensity of the polyene absorption was more pronounced at the longer wavelengths (69% decrease at 480 nm compared with 42% at 420 nm and 17% at 380 nm). The near-infra-red absorption was reasonably stable under our non-rigorous conditions, but gradually decreased in intensity with a half-life of about 2 h. Weak electron spin resonance (e.s.r.) signals, similar to those described by Tran[7] for thermally degraded PVC, were detected for DCM solutions of the polyenes. On addition of $SbCl_5$, these were reduced in intensity to a level that was near the limit at which they were detectable.

The relative intensities of the absorptions in the 500–750 nm region changed with time in a way that depended on the $[SbCl_5]/[\text{polyene}]$ ratio. In each case, the maxima at 590 and 650 nm decreased with time, while that at 720 nm increased to a maximum, then decreased. *Figures 3* and *4*, which are typical, summarize the changes that occurred over a 2 h period when 0.05 cm^3 of $SbCl_5$ were used.

When small portions of THF (increments of 0.01–0.02 cm^3) were added to a fresh solution of polyene/$SbCl_5$, the absorptions at 590, 650 and 720 nm changed progressively in ways that are described in *Figures 5* and *6*. Addition of the first aliquot caused A_{588} to decrease rapidly while A_{652} increased in intensity. Addition of further aliquots of THF brought about a reduction in A_{652} with a corresponding increase in A_{720} until it, in turn, decreased and was replaced by A_{780}. If no further

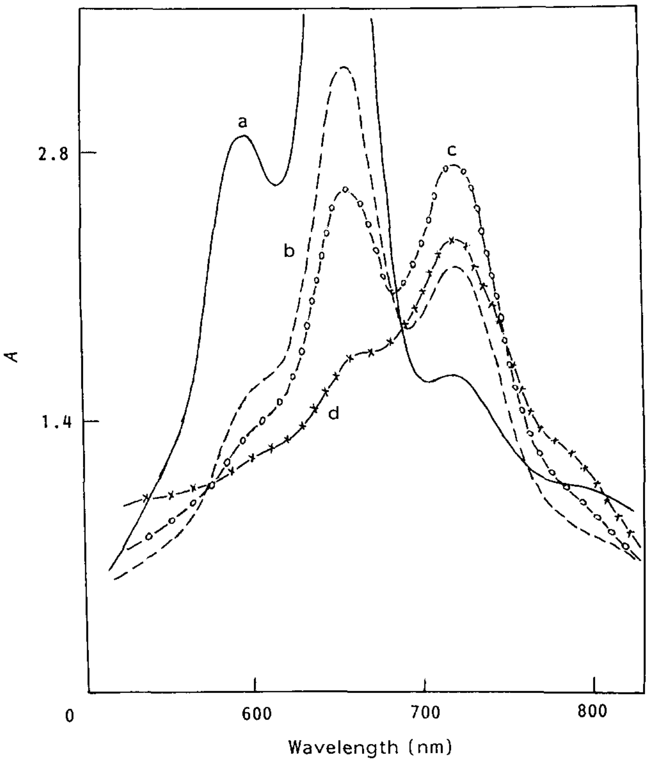


Figure 3 Changes of absorbance, *A*, with time for a DCM solution of CPVC-2 with $SbCl_5$ (10^{-4} M): (a) on mixing; and after (b) 20 min, (c) 40 min and (d) 120 min

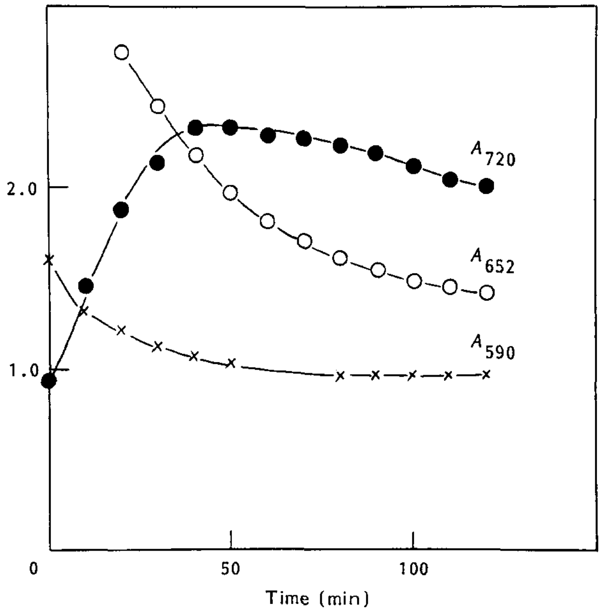


Figure 4 Changes in absorbance, *A*, with time at 590, 652 and 720 nm for the solution described in *Figure 3*

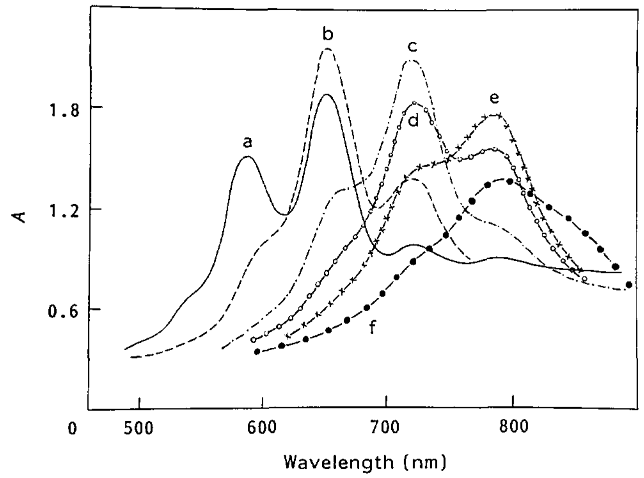


Figure 5 Changes in absorbance, A, for a DCM solution of CPVC-2 with $SbCl_5$ (10^{-4} M), immediately following addition of successive aliquots of tetrahydrofuran: (a) 0, (b) 0.01, (c) 0.03, (d) 0.05, (e) 0.06 and (f) 0.08 cm^3

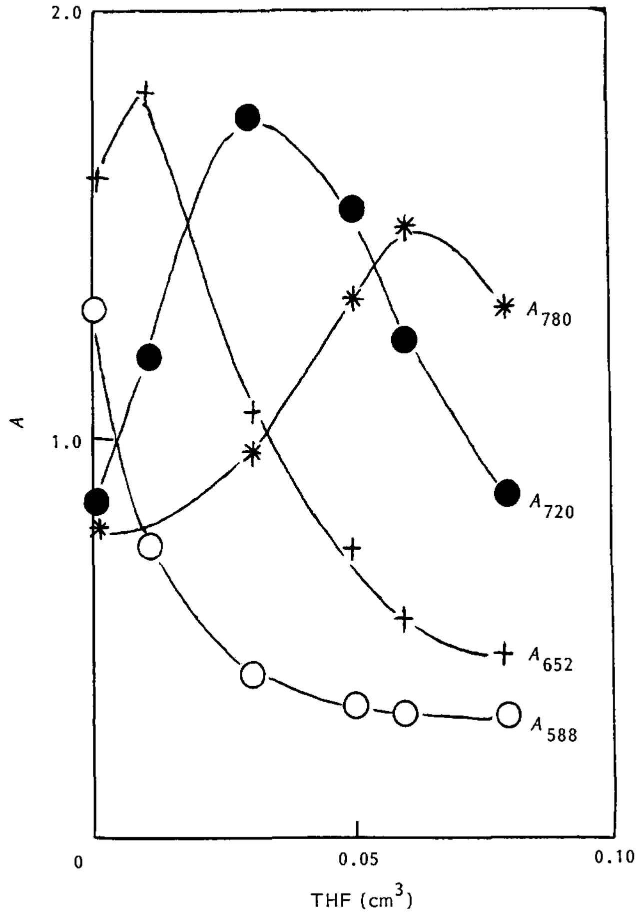
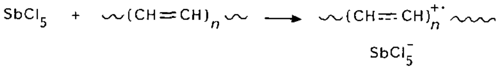


Figure 6 Changes in absorbance, A, at 588, 652, 720 and 780 nm for the solutions described in *Figure 5*

THF was added, the solution was fairly stable, the absorption at 780 nm gradually falling to about half its value over a 24 h period. When thiophene was added in place of THF, a similar pattern of behaviour was observed, but with differences in the relative intensities of the absorptions.

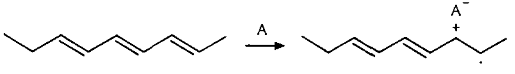
DISCUSSION

By analogy with our previous work[3,4] using $SbCl_3$ or $FeCl_3$ and the more recent model polyene systems synthesized and investigated by Spangler[5], it seems likely that the long-wavelength absorption produced at low $[SbCl_5]/[polyene]$ ratio is a consequence of the oxidative doping of polyene sequences in PVC, thus:

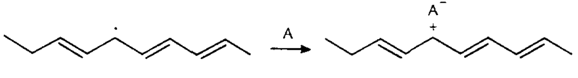


$$SbCl_5 + \sim(CH{=}CH)_n\sim \longrightarrow \underset{SbCl_5^-}{\sim(CH{=}CH)_n^{+\cdot}\sim} \qquad (1)$$

This results in the formation of a cation radical (polaron) species by preferential oxidation of the relatively longer polyene sequences, i.e.



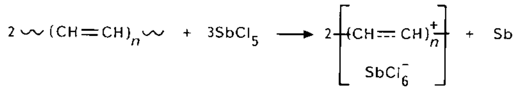
as well as the possible oxidation of existing neutral solitons ($S^{\cdot}$) to positive solitons (S^+), i.e.



Relative changes in the absorbance of the polyene sequences as well as the position of the very broad half-band absorption at 950 nm implicate polyenes with absorptions around 475 nm, i.e. with n in the range 10–14. The lack of a convincing e.s.r. signal accompanying this absorption may be explained by the reactivity of the soliton portion of the species in the presence of oxygen and HCl in accordance with the observations of Tran[7].

Further work is in progress to clarify this aspect of the problem, both in solution and in the solid phase.

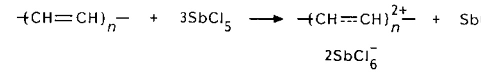
Stabilization of the anion by reaction with additional $SbCl_5$ molecules leads to the following stoichiometry:



$$2\sim(CH{=}CH)_n\sim + 3SbCl_5 \longrightarrow 2\left[\underset{SbCl_6^-}{(CH{=}CH)_n^{+}}\right] + SbCl_3 \qquad (2)$$

(I)

Further oxidation of polaron to bipolaron seems to be a preferred process:



$$-(CH{=}CH)_n- + 3SbCl_5 \longrightarrow \underset{2SbCl_6^-}{-(CH{=}CH)_n^{2+}-} + SbCl_3 \qquad (3)$$

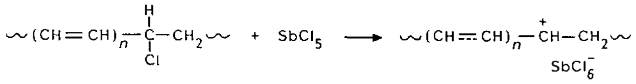
(II)

We ascribe the longest-wavelength absorption with λ_{max} around 950 nm to species **I** and the shorter-wavelength absorptions with maxima around 580, 650 and 720 nm to species **II** (bipolaron/polyene dication).

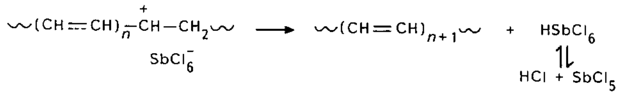
A very small increase in the concentrations of $SbCl_5$ shifts the absorption in the direction of species **II** and it seems likely, therefore, that in all our systems both polaron and bipolaron states are present. Although the concentrations of the polyene sequences that are long enough to sustain polaron and bipolaron states can only be approximated, it seems likely that even at the lowest concentrations of $SbCl_5$, which we have used, it may be in considerable excess.

The species responsible for the strong absorptions at shorter wavelengths with maxima around 450 nm are unknown, but one possibility, in view of the high $[SbCl_5]/[polyene]$ ratio, is that they may be due to aggregates or cyclic structures derived from the polyenes.

The gradual changes in the spectra attributed to species **II** over a period of about 2 h, which resulted in a stepwise shift of the absorption to longer wavelength, are consistent with an extension of the length of the conjugated polymer chain. It is likely that the $SbCl_5$, in addition to being an oxidant, acts as a catalyst for the dehydrochlorination process, i.e.



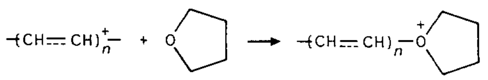
$$\sim(CH{=}CH)_n-\underset{Cl}{\overset{H}{C}}-CH_2\sim + SbCl_5 \longrightarrow \sim(CH{=}CH)_n-\overset{+}{C}H-CH_2\sim \quad SbCl_6^- \qquad (4)$$



$$\sim(CH{=}CH)_n-\overset{+}{C}H-CH_2\sim \quad SbCl_6^- \longrightarrow \sim(CH{=}CH)_{n+1}\sim + HSbCl_6 \rightleftharpoons HCl + SbCl_5 \qquad (5)$$

Detailed analysis of this system is complicated by uncertainty regarding the distribution of values of *n* in the original polyene, so that the absorptions attributed to species **I** and **II** have at least two major components with possible additional minor contributions from others. Slower changes, which resulted in decreases in absorbance over at least 24 h, were probably due to reactions with components of the atmosphere, since only conventional dry-box conditions were employed in assembling the systems, together with routine and careful, but non-rigorous, purification of the solvent.

The rather unexpected effect of adding relatively small amounts of THF or thiophene to these systems was also to shift the absorption maximum to longer wavelengths. This is most likely to be due to a catalytic effect of THF on the dehydrochlorination process described by equations (4) and (5), or a reaction in which THF and thiophene behave as nucleophiles towards the dication system and extend and localize the charge thus:



(6)

This behaviour is in accord with the observations of Spangler[2] concerning the relative charge-stabilizing effect of a thienyl compared with phenyl end-groups in model polaron and bipolaron systems.

Protonic doping of these systems using trifluoroacetic acid (TFA) produces similar but significantly different absorption both in DCM solutions and in the solid state. These will be described in detail in a separate communication.

ACKNOWLEDGEMENT

We thank the Government of the United Arab Emirates for the award of a Research Studentship to M.M.A.

REFERENCES

1 Spangler, C. W., Hall, T. J., Sapochak, L. S. and Liu, P.-K. *Polymer* 1989, **30**, 1166

2 Spangler, C. W., Liu, P.-K., Dembek, A. A. and Havelka, K. P. *J. Chem. Soc., Perkin Trans. 1* 1991, 799

3 Owen, E. D. and Brooks, S. R. *Polym. Photochem.* 1985, **6**, 21

4 Owen, E. D. and Msayib, K. J. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1833

5 Spangler, C. W., Hall, T. J., Sapochak, L. S. and Liu, P.-K. *Polymer* 1989, **30**, 1166

6 Shindo, Y., Read, B. E. and Stein, R. S. *Makromol. Chem.* 1968, **118**, 272

7 Tran, V. H., Guyot, A., Nguyen, T. P. and Molinié, P. *Polym. Degrad. Stab.* 1992, **37**, 209