

Results of the preliminary analysis of the POT data are shown in Fig. 1, which shows the *average* I-I distance *R* as a function of the iodine content in the samples. For some concentrations also a low and a high *R*-value could be discerned. As is seen the *R* varies between that of triiodides (2.93 Å) and that of solid I_3 (2.714 Å), the former dominating at the lowest concentrations and the latter being asymptotically approached at high concentrations. Assuming that the doping process leads to the formation of I_3^- ($P + 3/2 I_2 \Rightarrow P^+ + I_3^-$), one may use Fig.1 to calculate the variation of the I_1^- - and the I_2^- - content with the iodine concentration, giving the results of Fig.2

Fig.2 is very important and surprising: True doping, i.e. formation of I_3^- ions takes place only at iodine content below 0.3 (weight iodine/weight polymer). Further exposure of the polymer to iodine vapour evidently leads only to weight increase due to molecular I_2 , which appears to enter the material easily, but which only marginally will influence the electronic and conductive properties of POT

This finding in fact corroborates well with X-ray observations: At low iodine uptake the lattice parameters *a* and *b* have been reported [2] to vary linearly with the iodine content, *a* increasing and *b* decreasing, but such that an overall lattice expansion takes place. But these effects reverse and an overall moderate lattice contraction sets in as the uptake proceeds beyond 0.3. Our results strongly indicate that the initial lattice changes are directly related to the I_3^- -formation. Further uptake of molecular I_2 proceeds to give rise to a moderate lattice contraction. The results also show that the diffraction data of [2] will have to be reinterpreted. The reasonable assumption was made in that work that all iodine goes into the I_3^- -state, but Fig. 2 shows the I_3^- -content to saturate at a molar level of only 0.06-0.07 (referred to the monomer of the polymer), so that most of the iodine is in the form of I_2 at high doping level. The reason for the lattice contraction is not clear, however, but it is not unreasonable to think in terms of some complexing reaction

The studies indicate also the presence of interatomic distances about 3.5 Å and 5.8 Å, which tentatively could be interpreted as an I-S distance (S=sulfur in the thiophene backbone) and a next-nearest-neighbour I-I-distance in a linear I_3^- -ion.

Studies performed on PHT, PDoDT and on poly(dioctylbithiophene) (PDOT₂) and poly(dioctylterthiophene) (PDOT₃) have not yet been analysed quantitatively, but seem to be in gross agreement with those of POT.

References:

- [1] E.I.Samuelsen and J. Mardalen "The Structure of Polythiophenes" in H.S. Nalwa (Ed.) *Handbook of Organic Conductive Molecules and Polymers*, Volume 3 p. 87-120, John Wiley & Sons (1997)
- [2] T.J. Prosa, W.J. Winokur, J. Moulton, P. Smith and A.J. Heeger *Phys.Rev.BSI* 159 (1995)
- [3] U. Buontempo, D. Colognesi, A. Di Cicco, A. Filipponi, M. Nardone, P. Postorio, S. Mobilio, S.Pascarelli and F.D'Acapito *ESRF Annual Report 1994-1995 p. RI 78*
- [4] U. Buontempo, A. Di Cicco, A. Filipponi, M. Nardone, P. Postorio, *submitted to J. Phys. Chem.* (1997)

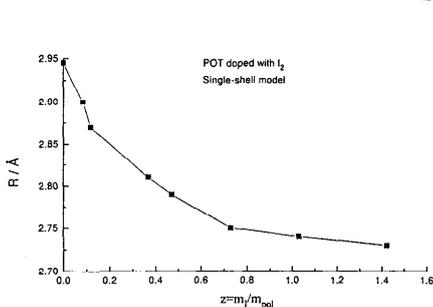


Fig 1

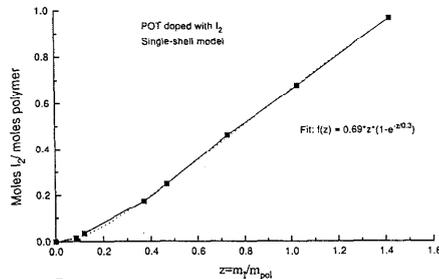
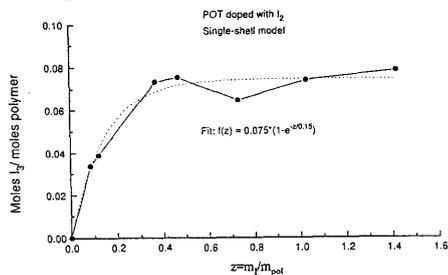


Fig 2