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Report:

Location of the counter-ions in I₂-doped conduct&polymers

Poly(alkylthiophene)s ((C₄HS-alkyl)_n) are conducting polymers that are reasonably well understood in their undoped form. The polymer main chains tend to order parallelly in a lamellar fashion, with the alkyl side chains extending normal to the lamellar planes [1].

For the *doped* polyalkylthiophenes the situation is different, however. There exists up till now no direct evidence for where and in which form the dopant molecules enter the polymer, but extensive X-ray diffraction studies have been performed on iodine &-doped poly(hexyl)-, poly(octyl)- and poly(dodecyl)-thiophenes (PHT, POT and PDoDT) [2]. Although these studies show that the polymer lattices expand upon doping, the dopant ions do not give rise to new reflections, and their location and molecular form in the lattice remain unsettled.

The present experiments aimed at characterizing the iodine molecular form and environment in doped polyalkylthiophenes using XAS spectroscopy.

EXAFS spectra of iodine in various forms were recently studied by Buontempo *et al* [3]. The interatomic distance in iodine solutions was observed to depend on the polarity of the solvent, being directly related to the solution colour, in another work by Buontempo *et al*. [4].

The K-edge of iodine is at 33.2 keV.

Various poly(alkylthiophene)s were studied in the present work, with POT studied in most detail. Cast films of thickness 40 - 100 μm were doped in iodine vapour at room temperature, and several doped films were put together to give an iodine content of the samples in the range of 20 - 40 mg I / cm². The iodine content was determined by weighing. To keep the doping level constant the samples were encapsuled in office tapes just after preparation.

Reference samples of crystalline triiodides were prepared. CsI₃, N(Methyl)₁I₃ and N(Butyl)₁I₃ with the latter the most used.

EXAFS absorption spectra were obtained at room temperature and at 40 K. For the subtraction of the atomic edge spectrum the data of ref. [4] was used. The low-temperature spectra differed from the RT spectra only by being less damped.

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_2 (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:

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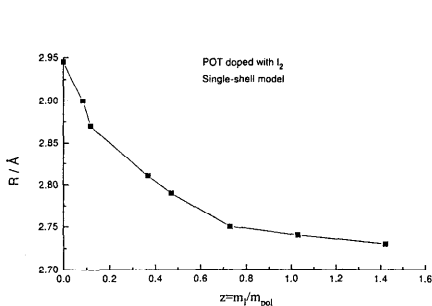


Fig 1

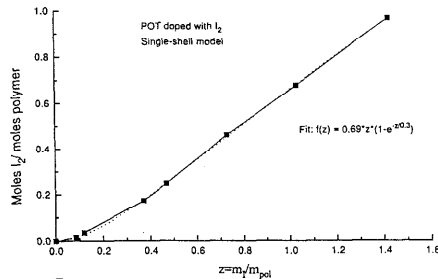
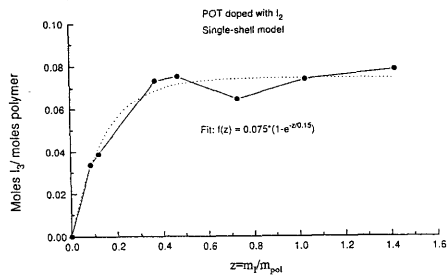


Fig 2