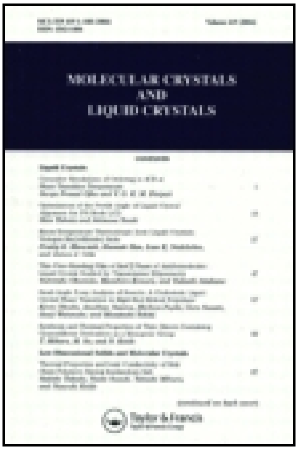

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IR Behaviour, Conductivity and Stability of $FeCl_3$-Doped polyparaphenylene $(p-C_6H_4)_x$

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IR BEHAVIOUR, CONDUCTIVITY AND STABILITY OF $FeCl_3$-DOPED POLYPARAPHENYLENE $(p\text{-}C_6H_4)_x$

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Abstract The correlation between σ_{dc} and the IR absorption ratio A_{1180}/A_{805} of the peaks at 1180 cm^{-1} and 805 cm^{-1} for $FeCl_3$-doped and pure $(p\text{-}C_6H_4)_x$, respectively, is presented. The stability of doped $(p\text{-}C_6H_4)_x$ is studied.

INTRODUCTION

It is known that doping of conjugated organic polymers such as polyacetylene (PA) and polyparaphenylene (PPP) causes new absorption peaks in the infrared (IR) spectrum accompanying the increase in conductivity (σ). The IR behaviour of undoped and AsF_5-doped PPP has been reported earlier.[1,2] Whereas the doping induced IR properties of PA have been accounted for by the presence of soliton defects, this interpretation cannot directly be transferred to PPP, which does not possess a degenerate ground state and is therefore not expected to accomodate single solitons. However, Bredas et al. have shown that soliton - antisoliton pairs could be stable in doped PPP and induce a quinoid structure of higher energy between the two defects.[3] A theoretical study of the IR spectra and structure of PPP has been presented by Rakovic et al.[4]

In our earlier studies of $FeCl_3$-doped PPP we have observed doping induced new peaks as indication for local deformations of the benzoid structure of PPP towards a quinoid one due to doping.[5] This paper presents the correlation we have found between σ_{dc} and the absorption ratio A_{1180}/A_{805} of the peaks at 1180 cm^{-1} and 805 cm^{-1} for the doped and pure polymer, respectively. This ratio becomes a measure of the amount of electrically active dopant whereas other methods such as atomic absorption in some cases detect electrically inactive contributions. The absorption ratio may therefore below saturating conductivities be used as a noncontact method for determining σ_{dc}, as in the ageing studies on PPP also presented in this work.

EXPERIMENTAL PROCEDURE AND RESULTS

Powder of PPP was polymerized from benzene using the method of Kovacic et al.[6] and the powder doped with $FeCl_3$ as described by Pron et al.[7] The dopant concentration was determined by atomic absorption. σ measurements were made using the four point method on pressed pellets. The IR studies were performed on a Perkin Elmer 983 spectrometer using KBr technique. The transmission level was measured setting the transmission of the empty spectrometer at 100 %. The absorption ratio A_{1180}/A_{805} of the peaks at 1180 cm^{-1} and 805 cm^{-1} for the doped and pure polymer, respectively, was

TABLE I Samples studied

Sample	σ_{dc} ($\Omega^{-1}cm^{-1}$)	Doping (mol%)*	A_{1180}/A_{805}
1	$<10^{-10}$	0	–
2	2×10^{-6}	0,8	0,03
3	7×10^{-5}	1,3	0,08
4	10^{-3}	2,0	0,12
5	7×10^{-2}	2,1	0,59
6	0,5	5,6	0,44
7	2	5,4	1,37

* atomic absorption

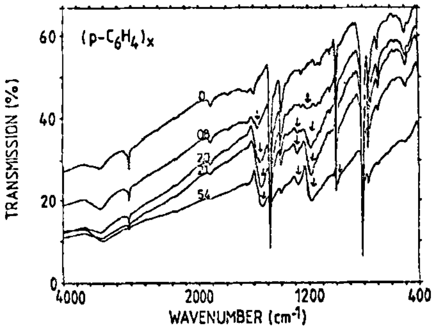

FIGURE 1. IR transmission of PPP for various doping levels. (↓) dopant induced peaks at 990, 1180, 1275 and 1530 cm^{-1}.

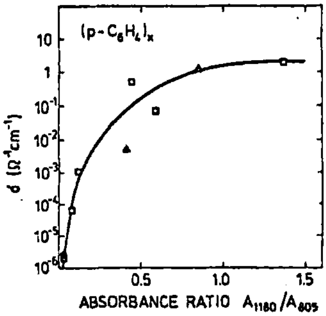

FIGURE 2. σ_{dc} of doped PPP plotted vs. IR absorbance ratio A_{1180}/A_{805}. (△▲) sample 7 after 1 yr in Ar or air respectively. (●) sample 2 after 1 yr in Ar.

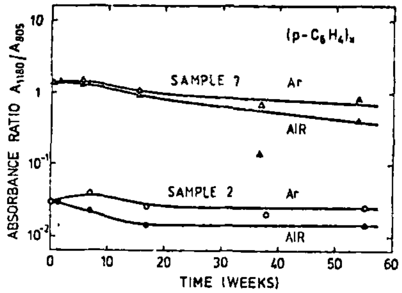

FIGURE 3. IR absorbance ratio A_{1180}/A_{805} as a function of time for doped PPP stored in Ar or air.

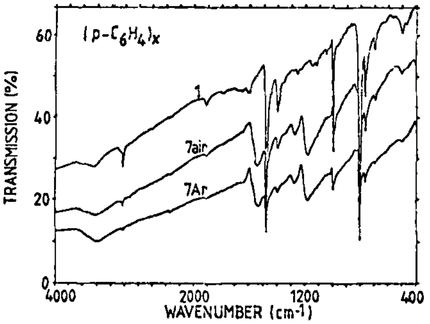

FIGURE 4. IR transmission of doped PPP (sample 7) after 1 yr in Ar or air compared to pure PPP (sample 1).

determined and plotted vs the measured σ. The samples studied in IR and σ measurements are listed in Table I. IR spectra of PPP of different doping level are shown in Fig. 1. Doping induced new peaks (↓) of increasing intensity coincide with those reported for AsF_5 doping.[1] A lower transmission with increasing σ is also seen in Fig. 1. The increasing absorption ratio A_{1180}/A_{805} with increasing σ is shown in Fig. 2. The stabilities for materials stored in Ar or air are presented in Figs 3 and 4 showing the decrease in absorption ratio A_{1180}/A_{805} and increase in transmission level, respectively, as a function of time. The corresponding conductivities of samples 2 and 7 after one year in Ar or air are shown in Fig. 2.

DISCUSSION

Using the same arguments as in the case of PA[8], we can state that the doping induced new peaks in the IR spectra are not due to specific vibrations of the dopant molecules or between the molecules and the polymer chain, because the peaks are the same for AsF_5- and $FeCl_3$-doping, but they are intrinsic vibrations of the polymer chain in the doped material. Recently we have found peaks induced by $HClO_4$-doping at 1275 and 1545 cm^{-1}, the peak at 1180 cm^{-1} being obscured by dopant material absorption. According to Racovics et al.[4] a peak at 1298 cm^{-1} close to our measured 1275 cm^{-1} is related to the quinoid structure of doped PPP. Thus the new IR peaks may be evidence for local deformations of the benzoid structure of PPP towards a quinoid one due to doping.[5] The decreased IR transmission with increasing doping in the whole frequency range studied is explained by free charge carriers.

Doped PPP is generally observed to be unstable but still more stable than PA. We have examined the stability both measuring the conductivity and the absorption ratio A_{1180}/A_{805} for comparing results. As shown in Figs 2 and 3 both methods give the same results. Storing in Ar gives good stability, the decrease in σ being hardly observable in one year. In air however, the stability is less good, as the conductivity decreases from the original value of $2\ \Omega^{-1}\text{cm}^{-1}$ to $7 \times 10^{-3}\ \Omega^{-1}\text{cm}^{-1}$. The conductivity decrease is also seen in the IR measurements both as an absorption ratio A_{1180}/A_{805} lowering as well as a transmission level rising. This indicates that the conductivity decrease upon ageing in doped PPP is due to slow deformation back to the benzoid structure.

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