

Electrical conductivity in poly-*p*-phenylene doped with antimony pentachloride and chlorosulphonic acid

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The electrical conductivity level of conjugated polymeric materials can be substantially changed by means of *n*- or *p*-type doping. Doped polymers can exhibit features of semiconductors and metals depending on the specific reaction of the dopant with the polymer and on the dopant concentration [1]. The formation of complexes of poly-*p*-phenylene (PPP) doping with antimony pentachloride, SbCl_5 , has been previously reported [2]. In this letter we present preliminary results on the enhancement of electrical conductivity after doping PPP with SbCl_5 and with another relatively weak electron acceptor chlorosulphonic acid, ClHSO_3 .

Poly-*p*-phenylene has been synthesized following the Kovacic method [3], which is based on a cationic polymerization of benzene using CuCl_2 as the oxidant and AlCl_3 as a catalyst. The polymer powder after exhaustive purification with hot HCl ($\sim 5\text{ M}$) and boiling water sintered at 0.75 GPa in the form of 0.5 to 0.7-mm-thick platelets at room temperature. The samples were exposed to an atmosphere of ClHSO_3 and SbCl_5 for different periods of time at room temperature. In the case of SbCl_5 , doping was carried out within a glass cell under 10^{-2} torr static vacuum. The relative increase in weight of the samples and the electrical conductivity using the four-probe method were measured independently under ambient atmosphere immediately after a selected doping time. Infrared spectroscopy, using the KBr method, and X-ray diffractometry were used to characterize the samples.

Fig. 1a illustrates the 400 to 1600 cm^{-1} region of the infrared spectrum for the synthesized PPP. The spectrum resembles that reported by other authors [4]. The strongest band at 800 cm^{-1} is attributed to the C-H out of plane deformation

mode for *p*-disubstituted phenyl rings. The bands at 690 and 760 cm^{-1} are related to monosubstituted phenyl rings (chain ends). From the ratio of the intensity of the 690 and 760 cm^{-1} bands to that of the 800 cm^{-1} band, according to a calibration curve for linear oligomers of *p*-phenylene [5], we estimate that the PPP chains should have at least nine phenylene rings. However, the insolubility and lack of melting of PPP do not allow a direct determination of molecular weight. Furthermore, the C/H + Cl = 1.54 ratio obtained (with 2 wt % chlorine) and the dark brownish colour of the powder support the infrared spectrum of SbCl_5 -doped PPP does not exhibit appreciable changes the corresponding spectrum of PPP doped with ClHSO_3 (Fig. 1b) shows additional bands indicating a chemical attack of the polymer. The above-mentioned monosubstituted bands practically disappear after the first hours of treatment with ClHSO_3 , suggesting that the initial attack produces a chemical reaction at the chain ends. This type of chain-end reaction would not substantially affect the conjugation length. The wide-angle X-ray diffractograms of SbCl_5 -PPP show a large loss of scattering intensity as a function of doping time (Fig. 2). This is due to the high mass-absorption coefficient ($800\text{ cm}^2\text{ g}^{-1}$ for SbCl_5) of the dopant intercalated within the polymer. Thus, after removing a thin $10\text{-}\mu\text{m}$ surface layer of the treated polymer, the original diffracted intensity is totally recovered. This result implies that doping takes place preferentially at the surface and that dopant diffusion into the sample proceeds slowly.

Fig. 3 illustrates the relative weight increase of the samples as a function of doping time with

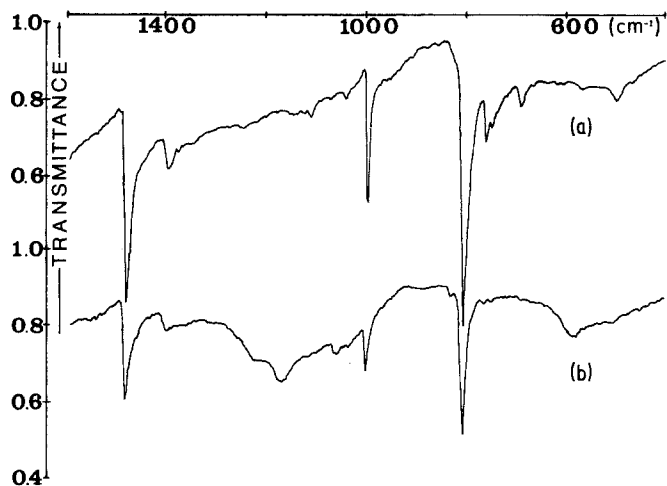


Figure 1 Infrared spectral region between 400 and 1600 cm^{-1} of poly-*p*-phenylene powder sintered with KBr. (a) Polymer as synthesized, (b) PPP after doping with ClHSO_3 for 24 h.

SbCl_5 . For the samples used, having a thickness of ~ 0.6 mm, ΔW remains below 10% after about 1 day of treatment. For a given doping time the weight increase is somewhat lower for ClHSO_3 than for SbCl_5 . Since doping proceeds from the outer surface towards the inner core, the measured ΔW for a given doping time depends critically on the sample thickness used. The electrical conductivity (σ) rise of PPP doped with SbCl_5 has been plotted as a function of ΔW in Fig. 4. We observe a remarkable enhancement of σ for the lower ΔW . The measured

conductivity of pristine PPP increases very rapidly from 10^{-14} up to $\sim 10^{-6} \text{ohm}^{-1} \text{cm}^{-1}$ for $\Delta W \leq 1\%$. Thereafter σ increases continuously with ΔW levelling off at values of $\sim 10^{-3} \text{ohm}^{-1} \text{cm}^{-1}$ for larger weight-increase values. The conductivity levels exhibited by PPP doped with ClHSO_3 are similar to those found by doping PPP with SbCl_5 . For instance a sample with $\Delta W = 4.3\%$ yields a σ value of $\sim 10^{-4} \text{ohm}^{-1} \text{cm}^{-1}$. This level of conductivity lies in the upper region of semiconducting materials. These levels are considerably lower than those reached by doping PPP with stronger acceptors like AsF_5 ($\sigma \sim 10^2 \text{ohm}^{-1} \text{cm}^{-1}$) [7].

During storage of the doped samples under ambient atmosphere a weight loss and a concurrent conductivity loss is observed. Fig. 5 depicts the variation of σ with storage time for two samples of PPP doped with SbCl_5 and ClHSO_3 , having similar initial σ values. After storage periods > 5 day values of σ for the samples tend

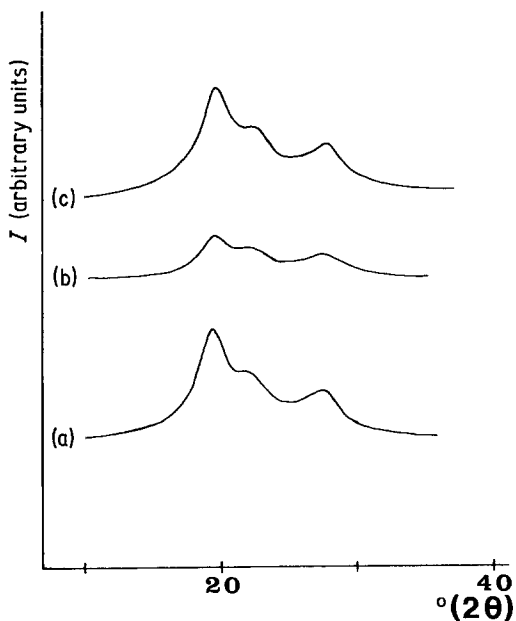


Figure 2 X-ray diffractograms using $\text{CuK}\alpha$ radiation from (a) platelets (0.75 mm thick) of PPP. (b) Sample a doped with SbCl_5 for 3 h (relative weight increase of $\sim 3\%$). (c) Sample b after peeling off a thin $10\text{-}\mu\text{m}$ layer.

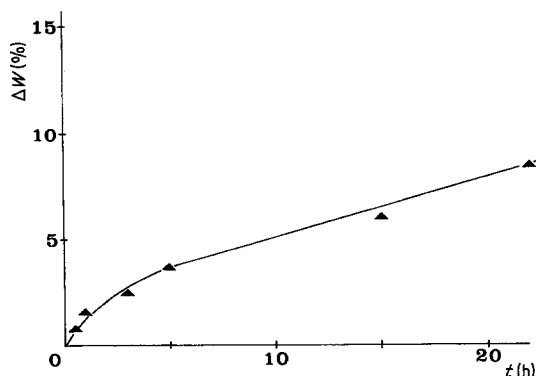


Figure 3 Relative weight-increase ΔW of platelets (~ 0.6 mm thick) of PPP doped with SbCl_5 as a function of doping time.

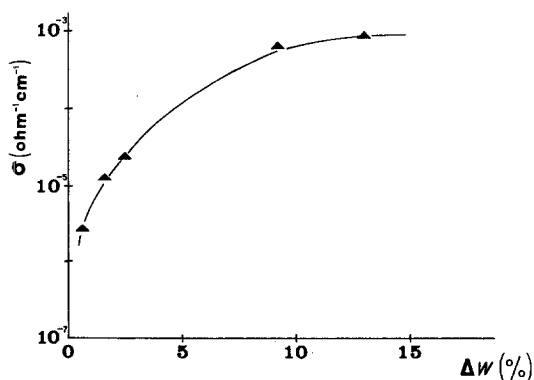


Figure 4 Variation of the electrical conductivity σ as a function of relative weight-increase ΔW of the PPP doped with SbCl_5 .

to level off. In the case of PPP doped with ClHSO_3 the data are more scattered and the rate of decrease for σ is slower than when doped with SbCl_5 . The larger rate of decrease for PPP doped with SbCl_5 may be due to the higher instability of this agent to air. Independent measurements of σ on PPP performed in an atmosphere of SbCl_5 lead to a maximum level of conductivity of $\sim 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$, which is reached in the first minutes of doping, remaining thereafter almost stable for prolonged periods of time [8]. This result contrasts with the data presented in Figs. 3 and 4 in which the increase of σ with ΔW , and hence with doping time, is much slower. This difference in behaviour between the conductivity

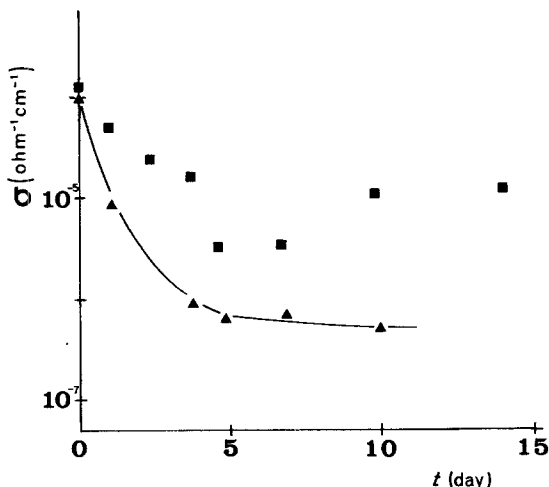


Figure 5 Electrical conductivity variation of samples of PPP doped with SbCl_5 (▲) and ClHSO_3 (■) as a function of storage time under ambient atmosphere.

of samples measured at ambient atmosphere and those measured *in situ* at dopant atmosphere could be attributed to the modification of the activity of the dopant species at the surface of the former samples. This could explain the observed difference between $\sigma \sim 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ in the former case and $\sigma \sim 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ in the latter case for low ΔW values ($< 1\%$).

In conclusion, doping of the synthesized PPP with SbCl_5 and ClHSO_3 provokes a notable enhancement in the electrical conductivity by 10 to 11 orders of magnitude. Doping of the material with ClHSO_3 is accompanied by a chemical attack of the polymer localized preferentially at chain ends, while doping with SbCl_5 does not produce appreciable changes in the infrared spectrum. For both dopants it is suggested that the formation of a charge-transfer complex is responsible for the conductivity enhancement observed. Mössbauer experiments to identify the ionic species are in preparation.

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