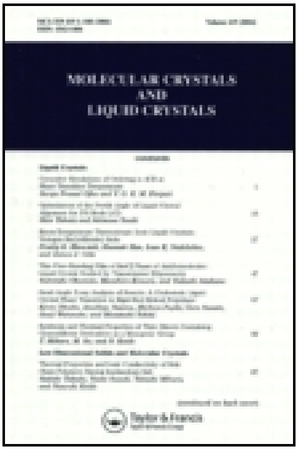

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ESR AND SOLID STATE HIGH RESOLUTION ^{13}C NMR IN AsF_5-DOPED POLY PARA-PHENYLENE

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Paramagnetic susceptibilities of AsF_5-doped poly(para-phenylene), $\{C_6H_4(AsF_5)_y\}_x$ were observed by the low field Shumacher-Slichter and X-band methods. The results were expressed by the sum of inverse-T (Curie) part and temperature-independent (Pauli) part. The Pauli part gradually appeared from about $y \sim 0.05$ and finally attained 1.5×10^{-6} emu/mole-carbon. This is half of that of polyacetylene. The Curie part lineally increased with y up to $y \sim 0.10$. This is in contrast to the case of polyacetylene. The Knight shifts corresponding to the susceptibilities were searched by the ^{13}C CP/MAS high resolution NMR method. The shift was not observed within the experimental accuracy of ±1 ppm.

INTRODUCTION

AsF_5-doped poly(para-phenylene) $\{C_6H_4(AsF_5)_y\}_x$ has been known to be an organic one-dimensional conductor, of which electrical conductivity reaches 500 Ω^{-1} cm^{-1}.1) The aim of this work is to study its electronic properties through magnetic methods of ESR and solid state high resolution ^{13}C NMR.

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The pristine polymers were synthesized with $CuCl_2$ and $AlCl_3$ as catalysts.[2] The doping was made by exposing the powders of the pristine polymers to AsF_5 atmosphere. Several samples of different doping levels were prepared by varying the doping time from 5 minutes to 24 hours. The same samples were used both in ESR and solid state high resolution ^{13}C NMR.

ESR

The ESR experiments were made with a low field Shumacher-Slichter method[3] as well as a conventional X-band method. The paramagnetic susceptibilities were obtained by integrating the observed ESR absorption lines. The standards used were the integrated intensities of ^1H NMR in the samples themselves for the Shumacher-Slichter method and those of ESR in a ruby crystal placed near the samples for the X-band. The Shumacher-Slichter method was carried out with a Q-meter spectrometer working at a typical frequency of 51.5 MHz.

With the above methods the temperature variation of paramagnetic susceptibility was measured between 4.2 and 300 K. At least fifteen data points were taken in this temperature range. All the data points were found to be expressed by the sum of a inverse-T (Curie) part and a temperature-independent (Pauli) part.

$$\chi = \chi_c + \chi_p$$

$$= \frac{N_c\,\mu_B^2}{k_B T} + \mu_B^2\,N(E_F), \quad \text{(emu/carbon-atom)}, \qquad (1)$$

where S=1/2 was assumed and N_c is the number of spins per carbon. The results were summarized in Figures 1a and 1b. Figures 1a and 1b show the temperature-independent and the inverse-T parts, respectively. The horizontal axis y is the number of dopant AsF_5 molecules per benzene. These ratios were directly determined by measuring the integrated intensities of both ^{19}F and ^1H NMR in the samples.

Figure 1a shows that the Pauli-like susceptibility appears at about $AsF_5/C_6H_4 \sim 0.05$ and finally attains 1.5×10^{-6} emu/mole-carbon. This behaviour is similar to that of trans polyacetylene reported by Ikehata et al.,[4] which is shown by a dashed line in the figure. For the trans-polyacetylene the horizontal axis is AsF_5/CH. The observed Pauli-like susceptibility of 1.5×10^{-6} emu/mole-carbon corresponds to a density of states at the Fermi level of 0.045 states/eV per

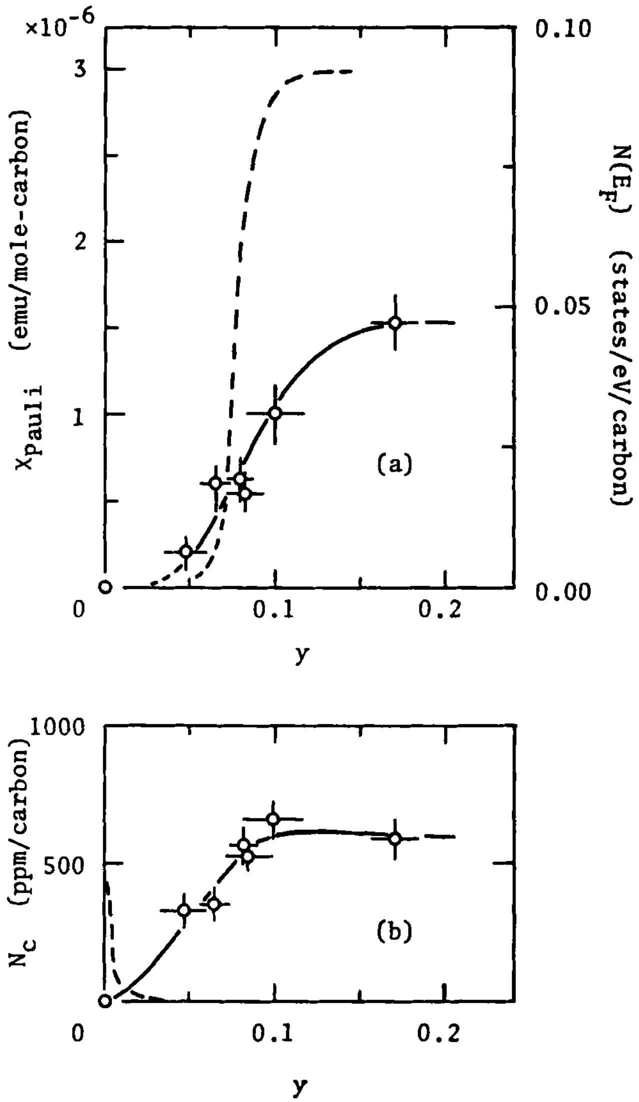

FIGURE 1 Paramagnetic susceptibilities of AsF_5-doped poly-(para-phenylene) as a function of AsF_5 concentration.
(a) Pauli part. (b) Number of Curie-type spins.
The dotted lines express the result for polyacetylene.4)
$y=AsF_5/C_6H_4$ or $/CH$.

carbon. This value is compared with 0.3 for Copper. This fact manifests that AsF_5-doped poly(para-phenylene) together with AsF_5-doped trans-polyacetylene is much like ordinary metals.

On the other hand, the behavior of the inverse-T part of the paramagnetic susceptibility is different between the two polymers. Although the inverse-T part of trans-polyacetylene rapidly disappears by addition of dopant AsF_5 molecules, that of poly(para-phenylene) slowly increases. The effective number of spins which appear by addition of one AsF_5 molecule is ≃0.03. The presence of spins may be connected with the benzene rings in poly(para-phenylene).

In the experimental results shown in Figures 1a and 1b, any difference was not observed between the Shumacher-Slichter and X-band methods. This fact shows that both the temperature-independent and inverse-T parts of the paramagnetic susceptibility are independent of frequency.

Recently, Peo et al.5) published magnetic susceptibility data on SbF_5-doped poly(para-phenylene) with the method of X-band ESR and magnetic balance. Their temperature independent (Pauli-like) part was more than two orders of magnitude smaller than ours, and inverse-T (Curie-like) part more than one order of magnitude smaller. Further studies will be required to find the cause of the difference.

HIGH RESOLUTION ^{13}C NMR

The high resolution ^{13}C NMR experiments were made with a CP/MAS method.6) The apparatus used was a home-built one operating at 13.3 MHz for ^{13}C NMR. The magic angle sample spinning head was of a Bullet type.7) The usually used spinning frequency was around 2 kHz.

Figure 2 shows an example of obtained spectra. The larger peak corresponds to site C_2 in Figure 3 and the smaller one site C_1. The obtained shift values of the peaks from TMS were summarized in Table 1. The data of a pure sample is consistent with those recently reported by Brown et al.8) In the last column of the table, the Pauli susceptibilities of doped samples are listed. These susceptibilities were already described in the section of ESR.

Some Knight shift is expected to be observed when a Pauli susceptibility is induced by the addition of dopant AsF_5 molecules. Actually in the case of AsF_5-doped polyacetylene, a Knight shift of 30 ppm was observed,9) accompanied with the appearance of Pauli susceptibility. For poly(para-phenylene), however, any change in the shift

Fig. 2

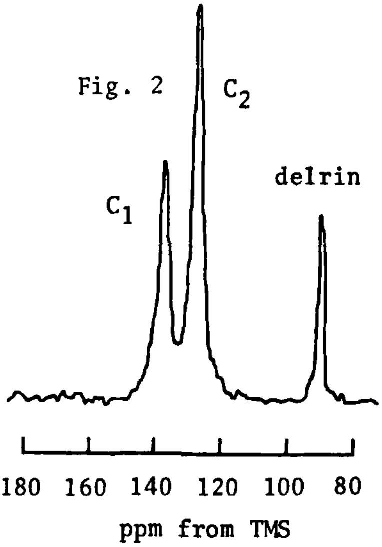

Fig. 3

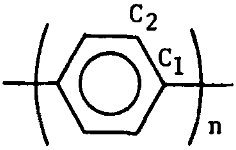

FIGURE 2 An example of solid state high resolution ^{13}C NMR spectra of poly(para-phenylene).

FIGURE 3 Structual formula of poly(para-phenylene).

Table 1 ^{13}C NMR line positions of C_1 and C_2 sites in poly(para-phenylene). Results on pure (undoped) and AsF_5-doped samples are listed. In the last column, the Pauli-susceptibilities χ_p are also shown.

AsF_5/C_6H_4	^{13}C NMR		χ_p
	Site C_1	Site C_2	
	ppm from TMS		$\times 10^{-6}$ $\frac{\text{emu}}{\text{mole-carbon}}$
undoped	137.4	127.6	———
0.05	138.4	127.2	0.2
0.08	137.7	127.2	0.6
0.17	137.0	127.0	1.5

value was not observed within the experimental accuracy.

There is a possibility that the Knight shifts have become smaller than the experimental accuracy. This case was shown to actually exist when it is assumed that the π-electron density at site C_1 is larger than that of C_2. In this estimation of Knight shifts a theoretical formula of Karplus and Fraenkel[10] was used. The chemical shifts were also found to be small when estimated through an empirical formula.[11] Further studies will be necessary to look for other possibilities.

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