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MAGNETIC PROPERTIES OF CONDUCTING POLYMERS

O.I. Aksimentyeva, V.T. Artym, O.I. Melnik and T.A. Plusnina

Lviv State Ivan Franko University, Ukraine

Magnetic susceptibility, electroconductivity and structure of polymer conducting layers of polyaniline and polyaminophenoles were studied in a wide temperature range. It was found that magnetic susceptibility depends on the doping level of polymer and the nature of doping agents. The obtained result suggested the existence of metallic states in highly doped conducting polymers.

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1. Introduction

Conducting polymers on the basis of aromatic compounds have attracted great attention because of their electrical properties and high thermostability. The investigation of conducting mechanism in polymeric conductors is an actual problem for the real technology application. Basic structural requirement for an appearance of metallic state of the polymer is that the chain contains a repetition unit with mobile carrier and presence of effective electron transfer (exchange) interaction between these unit groups [1, 2].

To define the nature of free carriers in polyaromatic systems the temperature dependencies of magnetic susceptibility, electric conductivity in connection with polymer structure must be studied.

2. Experimental

Polyaniline (PAN), polymetaaminophenole (PMAP), polyortoaminophenole (POAP) were obtained as electrodeposited films on the Pt, graphite surfaces at the current density 0.1–5.0 mA/sm^2, and synthesized by the interaction of aniline, *o*-, *m*-aminophenoles in aqueous sulfuric acid solution with ammonium persulfate at monomer–oxidant relationship 1:1. To obtain the basic form of PAN the precipitate was washed with 5% NH_4OH, distilled water, acetone and dried in vacuum. Doping procedure includes the treatment of PAN-base with 1N aqueous HCl, HFB_4, $HClO_4$ and saturated I_2 in chloroform solution. All the materials were identified by IR, UV spectroscopy and elemental analysis.

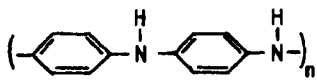
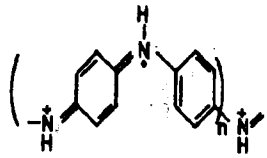
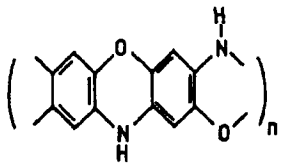
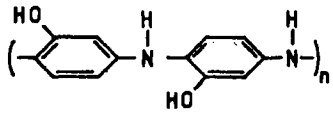
The X-ray diffraction analysis was performed on the DRON-2 diffractometer, where the Fe K radiation was used. Electron-microscopic analysis was performed on the UEMB-100 and REM-200 instruments. For EPR spectroscopy the radiospectrometer AE 4700 was used. Magnetic susceptibility was studied with magnetic microbalance in the 77–295 K temperature range.

3. Result and discussion

We studied the molecular and submolecular structure of polymer layers of PAN, POAP, PMAP polymerized on electrodes in aqueous acid solution and chemically synthesized [3]. According to the X-ray researching the diffraction patterns of the conducting polyaromatic polymers show a maximum, which contains reflections in its substructure with information about ordering of the polymers. This makes it possible to suppose that the structure of these materials is influenced by the existence of both amorphous and crystalline phases. Indexes of crystallinity calculated by means of the Bochard method is in the range 25–71% (see Table).

TABLE

Structure of polymer conductors.

Polymer	Molecular structure	X-ray reflection 2Θ	Index of crystallinity [%]
PAN_{base}		25.0; 26.5; 31.4	25
PAN_{doped}		18.7; 22.35; 25.6; 32.25	41
POAP		15.5; 16.7; 19.6; 26.0; 31.6; 35.2; 40.2	65
PMAP		48.0; 43.5; 34.5; 32.5; 21.5	23

According to the electron microscopy and electronography the PAN-films (600–800 Å) thickness consists of inhomogeneities by island nature (domains) on the 1–10 μm distance and the 0.1–3.0 μm diameter. The POAP films have the

fibre structure with linear stretched fibre. X-ray diffraction patterns of polymer films obtained on graphite surface show that macrochain molecules in the interface have a coplanar orientation with the basic plane of substrate.

Experiments, involving electron paramagnetic resonance for chemically synthesized PAN, POMP and PMAP, have shown that signal intensivity for PAN is more than two orders higher in comparison with other polyaromatic conductors.

The centres of EPR signal for PAN, POAP and PMAP are at 3371–3372 Hz, but the signal half-width is drastically different: for PAN a narrow signal is observed, while for POAP, PMAP its value increases 4–7 times. The loss of intensivity and boadering of EPR signals of polyaminophenoles correlates with these lower electrical conductivities in comparison with PAN.

On the basis of temperature dependencies of the aromatic polymers volume resistance it was established that conductivity of POAP, PMAP, undoped PAN and doped with iodine and sulfuric acid PAN is characterized by semiconductor behaviour with charge-transport activation energy 0.11–0.38 eV (see Fig. 1). PAN highly doped with HCl demonstrates the independence of the resistance in

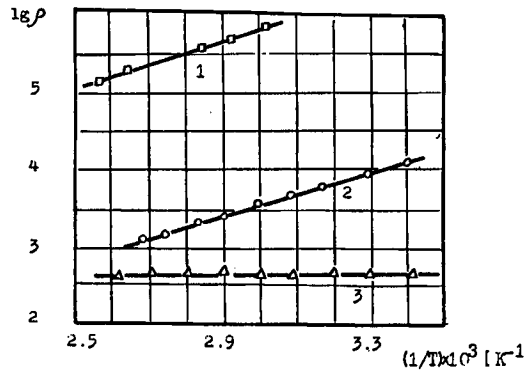


Fig. 1. Temperature dependence of resistance for the PAN doped by Y_2 (1), H_2SO_4 (2), HCl (3).

278–403 K range, which suggests the existence of metallic-type conductivity in this material.

We have studied the temperature dependencies of magnetic susceptibility of PAN, doped by different dopants, in the temperature interval 77–297 K and the effect of the magnetic fields on magnetic susceptibility changing. The obtained results are shown in Fig. 2.

As follows from the obtained data, for the HCl-doped PAN the Curie and Pauli spin paramagnetism in the temperature intervals 80–180 K and 200–300 K are observed. It was noted that spin paramagnetism is due to the electron conductivity and for the first time has been observed by MacDiarmid and Epstein [4] in chemically synthesized PAN. The temperature independence Pauli term is $\chi = 1.6 \times 10^{-4}$ sm^3/two aniline groups for HCl-doped PAN (7×10^{-5} e.m.u./two aniline groups for the HBF_4-doped), according to the result obtained by Tinaka

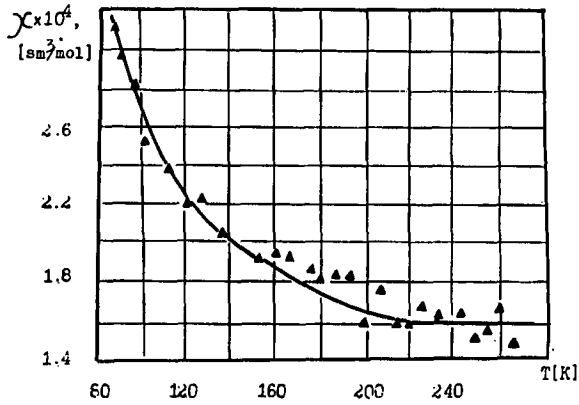


Fig. 2. Temperature dependence of magnetic susceptibility of PAN doped by HCl.

et al. [5]. This observation as well as resistance temperature independencies point out the metallic character of the polymer.

It was found that magnetic properties of doped polyaniline depend on doping agents and on the degree of oxiding; for H_2SO_4-doped PAN the diamagnetic effect took place in the range of temperature 80–290 K which is in the boundary interval with results obtained by Langer [6] (115–415 K).

4. Conclusion

The defining of magnetic properties of conducting polymer, in particular temperature dependencies of the magnetic susceptibility give information for the understanding of conducting mechanism in polyaromatic systems. Metallic character of conductivity is possible in highly acid-doped polyaniline by the electron delocalization along polymer chain and charge transfer among coplanar disposed aromatic rings.

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