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Chemical preparation, direct-current conductivity and thermopower of polyaniline and polypyrrole composites

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Polyaniline and polypyrrole composites were synthesized by doping during polymerization with a variety of organic and inorganic groups. Their direct-current (d.c.) conductivity was measured and their activation energy was estimated at room temperature. From thermopower measurements on polypyrrole composites a "metallic" p-type conductivity in the fibrils was revealed, although for polyaniline an n-type to p-type change of the carriers into the metallic "islands" was displayed at about 320 K. The introduction of the various groups, in addition to this change in the electrical properties, also resulted in conducting polymers capable of surface complexation with metal ions.

1. Introduction

Among conducting polymers, polyaniline and polypyrrole exhibit high conductivities [1–2] and unusually good chemical stability, which suggests that these polymers could be used as photochromic materials, as microelectronic elements, in the development of new photovoltaic elements, as chemical sensors, for photoelectrochemical reactions and for battery development. The aim of this work was the preparation and characterization of composite conducting polymers containing active agents; the introduction of functional groups such as $-SO_3H$ and $-COOH$ was another aim.

2. Experimental procedure

The monomer used was aniline (Merck AR), which was previously freshly distilled. Next, the monomer was polymerized in the presence of an oxidant in an ice bath, followed by soxhlet extraction for 36 h. The polymers were obtained as black powders; their conductivity depended strongly on the nature of the oxidant used and on the presence of an electrolyte or another polymer powder in the polymerization solution. The introduction of $-SO_3H$ groups was effected through the reaction of the $-NH$ groups of the polymer with freshly distilled chlorosulphonic acid at 5 °C. The $-COOH$ groups were introduced by copolymerization of m-aminobenzoic acid with aniline in the required proportion under the experimental conditions described above. Polypyrrole was synthesized by polymerization of the monomer as described in the literature [2]. Conductivity measurements, further characterization of the powders and crystallization experiments were performed as described elsewhere [3].

3. Results and discussion

The magnetic, transport and optical properties of conducting polymers imply that they are heterogeneous media. They usually consist of perplexed polymer chains of finite length with intrinsic defects, different sorts of connections between them and with the oxidizing or reducing dopants embedded randomly between the chains. Their conductivity depends on the concentration and on the kind of carriers (solitons, polarons or bipolarons), on the difficulty with which these carriers move along the chains, but mainly on the height of the energy barriers which a carrier must overcome to hop into one of the neighbouring chains. This explains why, although the conductivity in polymers can approach that of metals, the temperature dependence of polymers resembles the conductivity of semiconductors, characterized by a certain activation energy [4]. On the other hand, the thermopower depends mainly on the movement of the carriers along the polymer chains and is scarcely dependent on carrier hopping [5]. For these reasons the temperature dependence gives information about the interchain conduction of the polymer.

Structurally, polypyrrole can be treated as an inhomogeneous material consisting of thin fibrils with metal-like conduction, separated by thin potential barriers of poor electrical conductivity [6].

The conductivity of the polypyrrole samples varied from 2×10^{-3} to 30.6 S cm^{-1} as shown in Table I. The observed temperature dependence of the conductivities can be described by Mott's three-dimensional variable-range hopping model [7]. Near room temperature, the conductivity was characterized by activation energies, E_g, in the range 0.05–0.23 eV varying with the electrolyte and additive used, as shown in Table I. The conductivity of the polypyrrole

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TABLE I Polypyrrole preparations and their characteristics. The molar ratio of oxidant to pyrrole was 1:1, solvent triply distilled water

Electrolyte (% w/w)	Oxidant	Additives (% w/w)	Conductivity (S cm^{-1})	Thermopower (μV k^{-1})	E_g (eV)
–	$(NH_4)_2S_2O_8$	–	0.4	10.3	0.1
EHDP (33)	$(NH_4)_2S_2O_8$	–	1.4	11.3	–
$FeCl_3$ (30)	$(NH_4)_2S_2O_8$	–	2.1	12.8	–
$Bi(NO_3)_3$ (30)	$(NH_4)_2S_2O_8$	–	6.4	12.8	–
$KClO_3$ (87)	$(NH_4)_2S_2O_8$	–	17.3	–	–
	$(NH_4)_2S_2O_8$	CdS (6.4)	0.3	5.7	0.14
–	$FeCl_3$/pH = 2	–	30.6	8.9	0.05
–	$FeCl_3$/pH = 2	CdS (0.16)	0.1	15.5	0.18
–	$FeCl_3$/pH = 2	CdS (1.6)	4.9	10.1	0.10
–	$FeCl_3$/pH = 2	CdS (16.0)	7.1	12.3	0.06
–	$FeCl_3$/pH = 2	PVA (14)	10.0	5.7	–
–	$FeCl_3/FeCl_2$	–	0.03	25.0	0.14
–	$FeCl_3/FeSO_4$[a]	–	1.3	25.0	0.09
–	$FeCl_3/FeSO_4^+$	In_2S_3 (14)	0.02	60.0	0.20
–	$FeCl_3/FeSO_4^+$	PPTA-6 (24)	0.04	53.1	0.19
–	$FeCl_3/FeSO_4^+$	PPTA-11 (24)	0.02	51.5	0.16
–	$FeCl_3/FeSO_4^+$	PPTA-16 (24)	0.01	56.7	0.23
–	$FeCl_3/FeSO_4^+$	PVA (24)	0.2	65.3	0.23
–	$FeCl_3/FeSO_4^+$	PVA (14)	0.002	55.8	0.22
–	$FeCl_3/FeSO_4^+$	PVA (33)	0.3	62.1	–
	$FeCl_3/FeSO_4^+$	TiO_2 (14)	0.04	41.3	0.18
–	$FeCl_3/FeSO_4^+$	PPS (14)	0.04	38.1	0.13
–	$FeCl_3/FeSO_4^+$	PVC (14)	0.06	38.2	0.14

[a] Solvent CH_3OH, molar ratio oxidant $\{FeCl_3:FeSO_4 = 3.16:1\}$: pyrrole = 2.33:1, 4.C.

TABLE II Polyaniline preparations and their characteristics, with a molar ratio of oxidant to aniline of 1:1, and a solvent of triply distilled water

Electrolyte (% w/w)	Oxidant	Additives (% w/w)	Conductivity (S cm^{-1})	Thermopower (μV K^{-1})	E_g (eV)
–	$KClO_3$	–	0.04	– 20 to 55	0.19
–	$(NH_4)_2S_2O_8$	–	4.4	– 15 to 10	0.10
–	$FeCl_3$/pH = 2	–	5.6	– 8.8	–
–	$FeNO_3$/pH = 2	–	7.0	– 80 to 70	–
$Bi(NO_3)_3$ (25)	$FeNO_3$/pH = 2	–	5×10^{-6}	– 186.0	–
$Al(NO_3)_3$ (5)	$FeNO_3$/pH = 2	–	8.1	– 4.2	–
–	$FeNO_3$/pH = 2	PS–PH(O)OH, P(O)OH	0.06	8.0	0.18
–	$FeNO_3$/pH = 2	PS–PH(O)OH	0.13	70.0	0.16

composites with PPTA-x copolymer [8] decreased with increasing $(RO)_2P = O$ (x) content. The conductivity of the polypyrrole composites with CdS and polyvinyl alcohol (PVA) showed a rapid decrease for low contents of CdS and PVA. At higher concentrations however, the concomitant change of the polymer structure may be in the direction favouring conduction.

The thermopower was consistent with hole-like metallic conduction, ranging from 5.7 to 65.3 μV K^{-1} in accordance with experimental data published for polypyrrole doped to different levels by p-toluenesulphonabe [9].

Polyaniline has a different kind of heterogeneity to polypyrrole. It consists of discrete metallic "islands" made of a conducting fully protonated polymer randomly embedded into an insulating "sea" of non-protonated polyaniline [10]. The activation energy of the conductivity is related to the hopping between the "islands" and thus the connections between them, while the conduction into the "islands" may be deduced from thermopower data.

TABLE III Functionalization of polyaniline, with a molar ratio of oxidant to aniline of 1:1

Oxidant	Functional group (% mol per mol aniline)	Conductivity ($\times 10^2$ S cm^{-1})	E_g (eV)
$KClO_3$	O	3.5	0.19
$KClO_3$	$-SO_3H$ (15)	5.1	0.21
$(NH_4)_2S_2O_8$	O	440	0.10
$(NH_4)_2S_2O_8$	$-SO_3H$ (30)	1140	0.06
$(NH_4)_2S_2O_8$	$-SO_3H$ (50)	1190	0.06
$(NH_4)_2S_2O_8$	-COOH (30)	160	0.08

This "granular-metal" model predicts a temperature dependence of the conductivity that follows the equation: $\sigma = \sigma_0 \exp[-(T_0/T)^{\alpha}]$ where $\alpha = 1/2$, though for Mott's model $\alpha = 1/4$ [11]. The conductivities of our samples were best-fitted by an $\alpha = 1/2$ temperature dependence in agreement with the granular-metal model.

The electrical properties of various polyaniline samples is summarized in Tables II and III. The conductivities ranged from 5×10^{-6} to $11.9\,\mathrm{S\,cm^{-1}}$ and increased with increasing dopant concentration, reaching a plateau at about 50% of the content. The activation-energy values depended mainly on the original polymer and varied very little with the kind and the concentration of the dopant, in contrast to the observations in polypyrrole. This may be related to the different kinds of heterogeneities existing in the two polymers.

The thermopower revealed from the measurements had a low value, 80 to $4.2\,\mu\mathrm{V\,K^{-1}}$, which is characteristics of a metal, but it changed sign at about 320 K from n-type to p-type with increasing temperature. A similar behaviour has been observed in amorphous semiconductors [12].

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