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Comparison Between the Electric Conductivity of Polyhydroxamic Acids of Different Origin

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Summary. Polyhydroxamic acid (*PHA*) was prepared from polyacrylamide (*PAA*) and from polymethacrylamide (*PMAA*). It was found that *PHA* from *PAA* has the properties of a semiconductor when it reacts with some metals. *PHA* from *PMAA* has typical semiconducting properties when reacting with 1 mmol of ferric chloride, whereas its electric conductivity is somewhat lower when it contains 0.5 mmol of ferric chloride.

Keywords. Polyhydroxamic acid; Polyacrylamide; Polymethacrylamide; Electrical properties; Semiconductors.

Vergleich der elektrischen Leitfähigkeit von Polyhydroxamsäuren verschiedenen Ursprungs

Zusammenfassung. Polyhydroxamsäure (*PHA*) wurde aus Polyacrylamid (*PAA*) und Polymethacrylamid (*PMAA*) hergestellt. Bei der Reaktion mit einigen Salzen verhält sich *PHA* aus *PAA* wie ein Halbleiter. *PHA* aus *PMAA* hat typische Halbleitereigenschaften, wenn sie mit 1 mmol Eisenchlorid reagiert, während ihre Leitfähigkeit bei einem Eisenchloridgehalt von 0.5 mmol etwas niedriger ist.

Introduction

Some organic compounds show paramagnetic properties, *i.e.* they behave as semiconductors. *Eley* and *Parfitt* [1,2] have shown that some chelated compounds like phthalocyanin and copper-phthalocyanin have semiconducting properties. Organic compounds with paramagnetic properties are found among simple organic molecules [3,4], proteins [5] dyes [6] and chelated compounds as well as polymers [7]. *Wang*, *et al.* [8] have prepared blends of conducting polymers (polythiophene and polypyrrole in insulating host polymers like polystyrene and polycarbonate resins). *Yoshino et al.* [9] have produced polypyrrole-*PMMA* composites by hot pressing of a mixture of polypyrrole coated and non coated *PMMA* spheres at appropriate concentrations. Polypyrrole-*PE* composites have also been prepared by a similar method. Their electrical conductivity has been controlled over a wide range (10^{-7}–10 Ω^{-1}. cm^{-1}) by changing the concentration of the coated spheres. *Chen et al.* [10] have discussed the temperature dependence of the conductivity and

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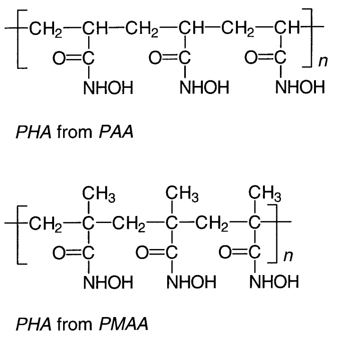
the structure of the composite. *Misra et al.* [11] have investigated semiconducting polymers (polypyrrole and polyaniline).

In this paper, the polymer chosen is polyhydroxamic acid (*PHA*) from polyacrylamide. It was found that *PHA* from polyacrylamide (*PAA*) has semiconducting properties when it reacts with some metals. *PHA* from polymethacrylamide (*PMAA*) has semiconducting properties when it contains higher concentrations of ferric ions.

Results and Discussion

From the introduction and from the above mentioned results it can be seen that organic compounds with semiconducting properties are either molecules containing hetero atoms such as oxygen, nitrogen, sulfur, *etc.* or substances with polar moieties like NO_2, SO_3H, SO_3Cl, OH, or NH_2OH. Polymers of moderate molecular weight that contain polar groups [17] or are linked to metals, oxides, or salts can also show semiconducting properties. Accordingly, polyhydroxamic acids from polyacrylamide and polymethacrylamide which are polymers containing polar groups (–NHOH) and which can be linked to metals and metal salts (*e.g.* Cu_2Cl_2 or $FeCl_3$) may have paramagnetic properties.

Compounds with semiconducting properties are characterized by specific electric conductivities between 10^{-12} and 10^{-2} $\Omega^{-1} \cdot cm^{-1}$ and by a linear relation between log ρ and $1/T$ ρ : electric resistivity; (T: absolute temperature).



PHA from *PAA*

PHA from *PMAA*

Scheme 1

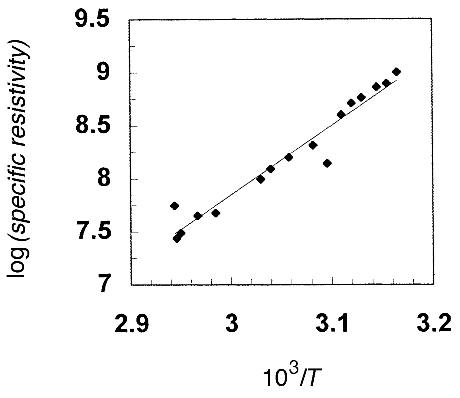


Fig. 1. Variation of specific resistivity with T^{-1} for polyhydroxamic acid from polyacrylamide + ferrous oxalate + cuprous chloride + cobalt acetate

Applying these criteria, it can be seen from Fig. 1 that polyhydroxamic acid prepared from polyacrylamide is a semiconductor. Its specific electric conductivity is $10^{-7}\Omega^{-1}\cdot\mathrm{cm}^{-1}$ at 70°C.

PHA from polymethacrylamide exhibits semiconducting properties at higher concentration of $\mathrm{FeCl_3}$ its specific electric conductivity ranging between 10^{-8} and $10^{-6}\Omega^{-1}\cdot\mathrm{cm}^{-1}$ at temperatures between 25 and 80°C (Fig. 4) Fig. 3 shows that, although the relation between $\log\rho$ and $1/T$ is linear for *PHA* from *PAA*, the specific electric conductivity is between10^{-10} and 10^{-12} at temperatures between 25 and 80°C, due to the lower $\mathrm{FeCl_3}$ content of this sample.

Figures 2 and 5 demonstrate that the relation between the electric current and voltage is ohmic for both *PHA* from *PAA* and *PMAA*.

Figure 6 shows that the relation between $\log\rho$ and $1/T$ for *PHA* from a copolymer of *AA* and *MMA* is linear. Since $\rho = 10^{-7}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ only at 80°C and the activation energy calculated for this compound is 113 kcal, this material shows semiconducting properties only at high temperatures. In Fig. 7 the relation between $\log\rho$ and $1/T$ is linear, and the specific electric conductivity between 25 and 85°C for the copolymer containing ferric chloride is between 10^{-7} and $10^{-5}\Omega^{-1}\cdot\mathrm{cm}^{-1}$; the activation energy calculated for this compound is 10.4 kcal. Accordingly, this material is a typical semiconductor. Figures 8 and 9 show that the relation between current and voltage for the copolymer is ohmic.

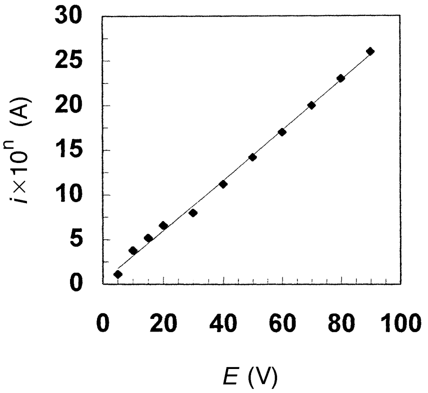


Fig. 2. Variation of current with voltage for polyhydroxamic acid from polyacrylamide films containing ferous oxalate, cuprous chloride, and cobalt acetate

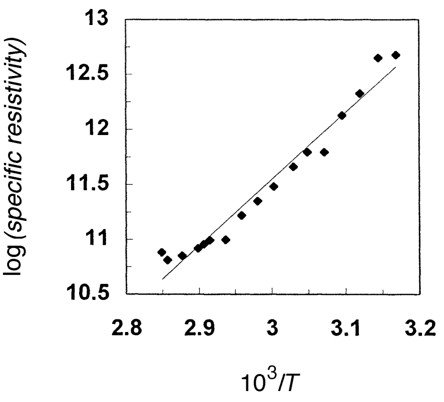


Fig. 3. Variation of specific resistivity of polyhydroxamic acid from polymethacrylamide containing 0.5 m mol ferric chloride with T^{-1}

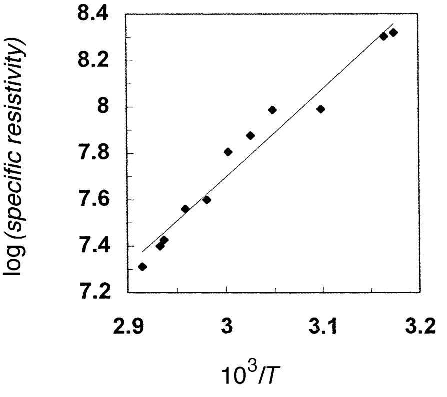


Fig. 4. Variation of specific resistivity with T^{-1} for polyhydroxarmic acid from polymethacrylamide containing lm mol ferric chloride

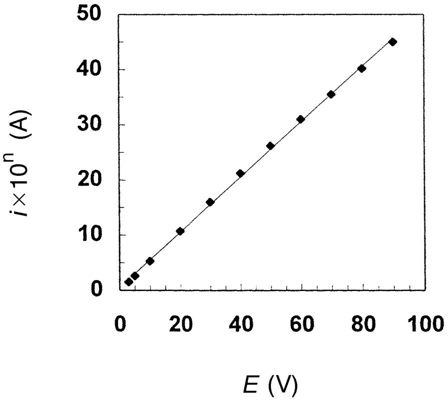


Fig. 5. Variation of current with voltage for *PHA* from polymethacrylamide containing 0.5 m mol ferric chloride

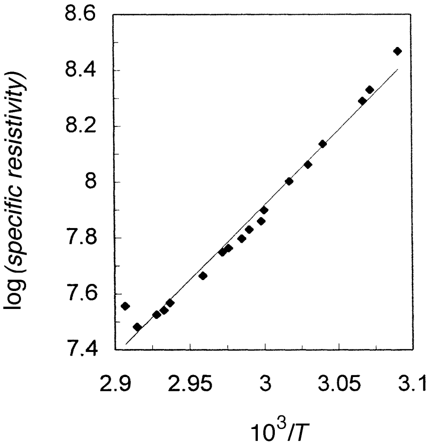


Fig. 6. Variation specific resistivity with T^{-1} for polyhydroxamic acid from a copolymer of acrylamide and methylmethacrylate

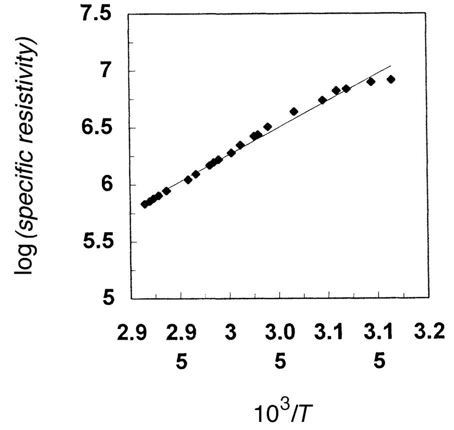


Fig. 7. Variation of specific resistivity for polyhydroxamic acid from a copolymer of acrylamide and methylmethacrylate + ferric chloride with T^{-1}

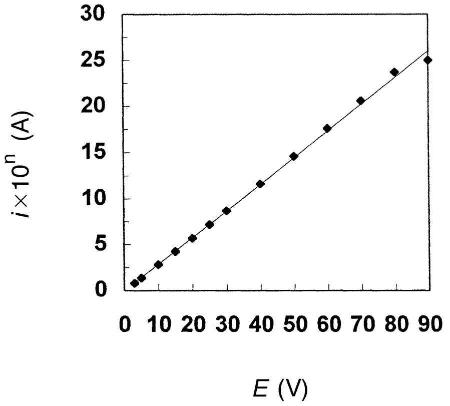


Fig. 8. Variation of current with voltage for polyhydroxamic acid from acrylamide and methylmethacrylate copolymer

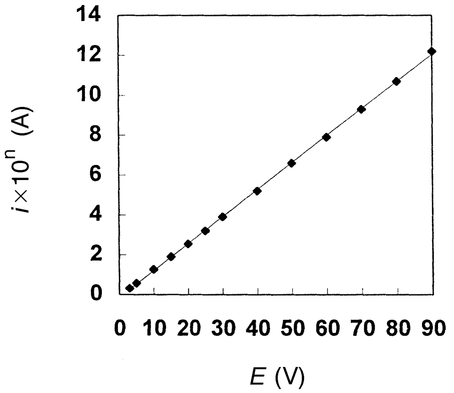


Fig. 9. Variation of current with voltage for polyhydroxamic acid from acrylamide and methylmethacrylate copolymer containing ferric chloride

The lower the activation energy, the more easily the substance can be activated to the semiconducting state. Compounds **2** and **3** demonstrate that the higher the concentration of $FeCl_3$, the more easily the substance becomes semiconductive. The values of the activation energies of compounds **4** and **5** show that the activation energy drops heavily when 1 mmole of $FeCl_3$ is added.

Compound	Activation energy[a]
PHA from *PAA* + $Fe(COO)_2$, Cu_2Cl_2, and $Co(CH_3COO)_2$ (**1**)	21.3 kcal
PHA from *PMAA* + 0.5 mmol $FeCl_3$ (**2**)	21.5 kcal
PHA from *PMAA* + 1 mmol $FeCl_3$ (**3**)	7.14 kcal
PHA from a copolymer of *AA* and *MMA* (**4**)	113 kcal
PHA from a copolymer of *AA* and *MMA* + 1 mmol $FeCl_3$ (**5**)	10.4 kcal

[a] Calculated according to *Arrhenius* from $\rho = \rho_o \exp(-E/RT)$

Experimental

Preparation of polyhydroxamic acid from polyacrylamide

The method of preparation has been described before [12]. To 20 g of polyacrylamide in 300 ml of water, 69.5 g (1 mol) of hydroxylamine hydrochloride were added. After stirring for 30 min at room temperature the *pH* was adjusted to ≥ 12 by successive addition of 55–65 g of sodium hydroxide. After 24 h, during which time ammonia evolves, the solution is rendered acidic by addition of 3 N HCl ($pH = 1-3$). 0.5 mmol/g of polymer of cuprous chloride, ferrous oxalate, and cobalt acetate were dissolved in 50 ml of water and added to the prepared mixture. The polymer is separated after reaction with the salts, washed with water and alcohol, and dried at low temperature. A pellet of 1 mm thickness of the salt was prepared.

Preparation of methacrylamide

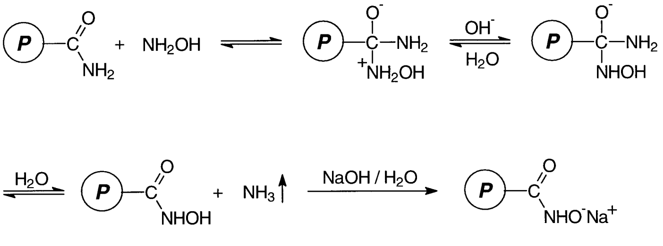
50 g (0.5 mol) of methylmethacrylate (*MMA*) and 90 ml of concentrated ammonia solution (specific gravity 0.88) were mixed in a round bottomed flask. After standing with occasional shaking for 1–2 days (until homogeneity; a longer period of standing is not harmful), the mixture is distilled. The method described makes use of a procedure for preparing acetamide from ethylacetate [13].

Preparation of polymethacrylamide

25–50 g of *MAA* were mixed with 100 ml of chloroform and 0.25–0.5 g benzoyl peroxide in a round-bottomed flask. After reflux for 20 min, the polymer was separated by distillation.

Preparation of polyhydroxamic acid from PMAA

The same procedure as for the preparation of *PHA* from *PAA* was followed. After acidification of the mixture to *pH* 1–3 with 3 *N* HCl, the polymer was separated by filtration. Two fractions of the



Scheme 2

polymer were dissolved in dichloromethane. To the first fraction, 0.5 mmol of $FeCl_3$ per gram of polymer were added. To the second fraction, 1 mmol of $FeCl_3$ per gram of polymer was added. The ferric salt solutions of *PHA* from *PMAA* were poured in petri disheds; films of 1 cm diameter and 1 mm thickness were obtained.

Preparation of a copolymer of acrylamide and methylmethacrylate

45 g of acrylamide and 5 g of methylmethacrylate were mixed in a round-bottomed flask. The contents of the flasks were dissolved in 100–200 ml of water, and 3 g of potassium persulfate were added. After mounting a reflux condenser, the contents were heated at 40°C for 15 minutes. The copolymer was obtained by distillation. The polyhydroxamic acid from the copolymer was prepared by the same method used for the preparation of *PHA* from polyacrylamide.

Measurement of the specific electric conductivity of the polymers

The specific electric conductivity of thin films of the polymers was measured by the method mentioned of *Eley* and *Parfitt* [1,2][1]. The thin film of 1 cm diameter and 1 mm thickness was tightly adjusted between the plates of two copper electrodes of an electric cell. The cell was put in an electric furnace. This electric cell was connected to a battery and an electrometer, forming an electric circuit. The electric conductivity was either measured directly by the electrometer, or from the measurements of the voltage and the electric current through the electric cell. The temperature of the electric furnace was measured by a thermocouple.

Measurement of molecular weight

The average molecular weights ($\bar{M}_n$) of polyacrylamide and polymethylmethacrylate were determined *via* viscosity measurements employing an *Ubbelohde* viscosimeter. The following relations were used: *PAA*, $[\bar{\eta}]_{30^\circ} = 6.8 \times 10^4[\bar{M}_n]^{0.66}$ [14, 15]; *PMAA*:$[\eta]_{30^\circ} = 0.94 \times 10^4[\bar{M}_n]^{0.76}$ [16]. The following values were obtained: PAA, $\bar{M}_n = 735.2$; *PMMA.*, $\bar{M}_n = 3880$; *PMAA,* $\bar{M}_n = 3315$.

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