

The resistivity of the nitroaryl and aminoaryl derivatives of cellulose

*G. ČÍK, ^bF. ŠERŠEŇ, and *A. BLAŽEJ

**Department of Textile, Pulp, and Paper, Slovak Technical University,
CS-812 37 Bratislava*

^b*Institute of Chemistry, Komenský University,
CS-832 32 Bratislava*

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The resistivity of some synthesized nitroaryl and aminoaryl derivatives of cellulose prepared by condensation of aromatic aldehydes with hydroxyethyl-cellulose was investigated. The temperature dependence of resistivity of the prepared derivatives obeys the relationship valid for semiconductors. The values of resistivity depend on character of the present chromophore and the high values of resistance are reached in case the polymer contains only a nitroaryl group. The simultaneous presence of acceptor and donor group reduces the resistivity by six decimal orders. The values of the resistivity activation energies of the prepared derivatives vary in the range 0.42—0.63 eV.

Исследовалось удельное сопротивление синтезированных нитроарил-аминоарил-производных целлюлозы, полученных конденсацией ароматических альдегидов с гидроксиэтилцеллюлозой. Температурная зависимость удельного сопротивления полученных производных подчиняется соотношению, действительному для полупроводников. Значения удельного сопротивления зависят от характера присутствующего хромофора, причем высокие значения сопротивления достигаются в случае, если полимер содержит только нитроарильную группу. Одновременное присутствие акцепторной и донорной групп ведет к понижению удельного сопротивления на 6 порядков. Величины энергий активации удельного сопротивления полученных производных лежат в промежутке от 0.42 до 0.63 эв.

Recently, an increased attention was paid to the polymers which contain in their main or side chain strong donating or accepting groups able to form inter- or intramolecular charge-transfer complexes [1]. However, the resistivity was studied only for some known systems. It is known that such purposeful orientation of chromophores chemically bonded to polymer chain gives rise to the origination of greater conformational disturbances. Thus different orientation and concentration effects arise, which manifests itself by the formation of charge-transfer complexes

even if the low-molecular compounds do not form any complexes. The polymers able to form charge-transfer complexes represent potential materials suited to applications in different lines. Their electrical properties are especially interesting because they predetermine them for application in the region of electrotechnics as insulants, semiconductors, superconductors as well as in electrophotography. Only few papers are concerned with complexes involving charge transfer on cellulose carriers. The synthesis of trinitrobenzyl and trinitrophenyl ethyl ethers of cellulose which are insoluble polymer acceptors able to form n -complexes with aromatic amino compounds has been described in paper [2]. However, no derivative forms π -complex. Snyder and Welch [3] synthesized an insoluble derivative, i.e. 3,5-dinitrobenzoylcellulose which formed both n - and π -complexes with different low-molecular aromatic donors.

The results of the study of the resistivity of 4-nitrobenzaldehyde hydroxyethylcellulose acetal (*I*), 4-aminobenzaldehyde hydroxyethylcellulose acetal (*II*), (4-diazoniobenzaldehyde chloride) hydroxyethylcellulose acetal (*III*), and 4-*N*-dimethylaminobenzaldehyde hydroxyethylcellulose acetal (*IV*) are presented in this paper. These cellulose derivatives were prepared by condensation of aromatic aldehyde with hydroxyethylcellulose (products *I* and *IV*) and subsequent reduction of the nitro group (product *II*) succeeded by diazotation of the amino group (product *III*).

Experimental

Water-soluble hydroxyethylcellulose Natrosol 250 GR (Hercules) with average degree of polymerization $DP_v = 152$, molar degree of substitution $MS = 2.5$, and degree of substitution $DS = 1.50$ was used for synthesis. The synthesis of the derivatives was carried out by the modified method involving condensation of aromatic aldehyde with hydroxyethylcellulose [4]. The reduction of the nitro group was performed according to the method described in paper [5].

The electronic absorption spectra were measured with a spectrophotometer Specord UV VIS (Zeiss, Jena). The infrared spectra were taken with a spectrophotometer IR-71 (Zeiss, Jena) by using KBr tablets.

The resistivity of the derivatives of hydroxyethylcellulose was measured in the temperature range 21–120 °C by the use of pressed powder samples. Before pressing, the samples were carefully homogenized in an agate mortar. The pressing was carried out with a press DP-36 (E. Hammerschmidt, GDR). The samples in the form of tablets of 12 mm diameter and approximately 1 mm width were prepared *in vacuo* ($p \approx 1$ Pa) at the pressure of 6.4×10^8 Pa. The electrodes were arranged in the sandwich form on the samples. They were put on the samples by evaporation of gold *in vacuo* ($p \approx 1 \times 10^{-3}$ Pa). The deposition of electrodes was performed by means of a High Vacuum Pumping Unit 35 (LP, CSSR) where the preparation for metal depositing was placed in a thick-walled glass bell. The measurements of direct current resistivity were performed with the equipment described in paper [6].

The electrical current was measured with an electrometer which was equipped with a vibration condenser of the type Schwingkondensator-Voltmeter VA-J-52 (RFT, GDR). All measurements were carried out in nitrogen atmosphere or *in vacuo* ($p \approx 1$ Pa). The obtained results were processed by the method of least squares.

4-Nitrobenzaldehyde hydroxyethylcellulose acetal (I)

Hydroxyethylcellulose (25 g) was dispersed in 350 cm³ of concentrated acetic acid and gradually heated to reflux. 4-Nitrobenzaldehyde (25 g; 0.165 mol) was added under constant stirring and subsequently the solution consisting of H₂SO₄ (1 cm³) and acetic acid (10 cm³) was admixed in parts. The reaction proceeded on oil bath under reflux for 3 h.

The reaction finished, the dark-brown product was precipitated with water and yet three times purified by precipitation into water. After drying *in vacuo*, we obtained 12.4 g of product ($w_i(\text{found})$): 56.56 % C, 3.14 % H, 5.64 % N, 34.66 % O). The product was soluble in acetone, chloroform, dimethylformamide and insoluble in water.

4-Aminobenzaldehyde hydroxyethylcellulose acetal (II)

4-Nitrobenzaldehyde hydroxyethylcellulose acetal (I) (5 g) was put into 35 cm³ of ethanol and the mixture was heated to reflux. Then sodium dithionite (8 g; 0.046 mol) dissolved in 35 cm³ of water was gradually added in the time interval of 30 min under constant stirring. The reaction was terminated after 2 h. The reaction product which passed into solution in the course of reduction of the nitro groups was precipitated with ethanol. The product was purified by dissolving in water and twofold reprecipitation with ethanol. After drying *in vacuo*, we obtained 3.6 g of dark-brown product ($w_i(\text{found})$): 21.67 % C, 2.1 % H, 74.08 % O, 2.24 % N).

(4-Diazoniobenzaldehyde chloride) hydroxyethylcellulose acetal (III)

The amino derivative of hydroxyethylcellulose (II) (2.5 g) was dissolved in 10 cm³ of water and 5 cm³ of 2 M-hydrochloric acid. After cooling to 0 °C, we successively added 0.5 M aqueous solution of sodium nitrite. The excess of free nitric acid was indicated by iodide-starch test paper. The product was precipitated with ethanol and allowed to dry in free. Thus we obtained 1.9 g of brown-violet product which was soluble in water ($w_i(\text{found})$): 22.46 % C, 2.30 % H, 73.32 % O, 1.92 % N).

4-N-Dimethylaminobenzaldehyde hydroxyethylcellulose acetal (IV)

Hydroxyethylcellulose (20 g) was put into 200 cm³ of concentrated acetic acid and heated under constant stirring to reflux till the polymer entirely dissolved. 4-*N*-Dimethylamino-

benzaldehyde (20 g; 0.134 mol) dissolved in acetic acid (150 cm³) was gradually given into the solution and subsequently the solution consisting of sulfuric acid (1 cm³) and acetic acid (10 cm³) was added. The reaction proceeded under reflux for 3 h. The reaction finished, the dark-brown product was precipitated with acetone. The product thus obtained was purified by dissolving in water and threefold reprecipitation with acetone. After drying *in vacuo*, we obtained 16.5 g of the product which was soluble in water and dimethylformamide ($w_i(\text{found})$: 49.90 % C, 4.81 % H, 4.37 % N, 41.0 % O).

Results and discussion

The electronic absorption spectra of the synthesized derivatives of cellulose are represented in Figs. 1 and 2 and in Table 1. The modification of hydroxyethylcellulose manifests itself in the electronic absorption spectra by new absorption bands while the positions of the maxima are given by the present chromophore. Though the products are coloured, the absorption maxima are shifted under $\lambda = 300$ nm, which is in good agreement with the absorption spectra of the low-molecular

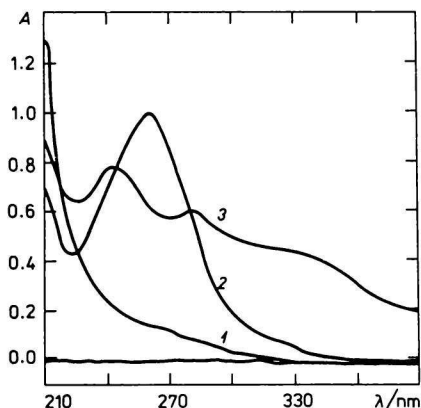


Fig. 1. Electronic absorption spectra of the derivatives of cellulose.

1. Hydroxyethylcellulose (water); 2. 4-nitrobenzaldehyde hydroxyethylcellulose acetal (methanol); 3. 4-aminobenzaldehyde hydroxyethylcellulose acetal (methanol).

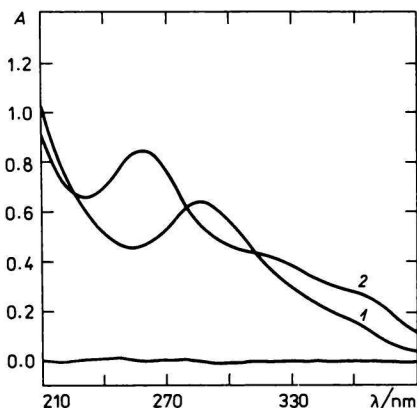


Fig. 2. Electronic absorption spectra.

1. (4-Diazoniobenzaldehyde chloride) hydroxyethylcellulose acetal (water); 2. 4-N-dimethylaminobenzaldehyde hydroxyethylcellulose acetal (methanol).

aromatic nitro and amino model compounds or diazonium salts [7]. On the other hand, we may observe some more remarkable differences in the form of absorption bands of the prepared derivatives. These differences appear especially with product *II* and involve a shift in absorption maximum in bathochromic sense and a sensible hyperchromic shift in the right-hand shoulder.

Table 1

Resistivity of the synthesized derivatives of cellulose

Product	$\frac{\lambda_{\max}^a}{\text{nm}}$	DS _{aryl} ^b	n(C)/n(O) ^b	$\rho(25^\circ\text{C})/(\Omega\text{ m})^c$	$\frac{\Delta E}{\text{eV}}$	$\rho(25^\circ\text{C})/(\Omega\text{ m})^d$	Note
I	212 267 (methanol)	1.65	1.63	1.03×10^{15}	0.42	1.03×10^{15}	—
II	242 283 (methanol)	0.607* 0.41'	0.29	1.28×10^9	0.63	1.28×10^9	—
III	284 (water)	0.57	0.30	8.07×10^{11}	—	1.40×10^4	Temperature instable sample
IV	259 (methanol)	1.305	1.21	2.51×10^{14}	0.49	1.42×10^{11}	—
Mixture of I and IV n(I):n(IV)=1:1	—	—	—	1.11×10^{10}	0.52	2.06×10^9	—

a) Saturated solution; b) calculated according to elemental analysis; c) resistivity measured at 25 °C in inert atmosphere; d) resistivity measured at 25 °C in air; e) calculated according to elemental analysis from total content of nitrogen; f) determined by diazotation.

Table 2

Infrared spectra of the synthesized derivatives of cellulose

Product	$\tilde{\nu}/\text{cm}^{-1}$			
	$\nu_{\text{as}}(\text{NO}_2)$	$\nu(\text{phenyl})$	$-\text{N}\equiv\text{N}$	>N-Ph-
<i>I</i>	1518	1610	—	—
<i>II</i>	1518	1610	—	—
<i>III</i>	1518	1600	2120	—
<i>IV</i>	—	1595	—	820

As derivative *II* was prepared by reduction of the nitro groups of derivative *I*, we may expect that the reduction does not proceed completely because of reaction conditions irrespective of the fact that dithionite is known as a strong reduction agent for nitro groups. The presence of the nitroaryl and aminoaryl chromophores in derivative *II* may thus give rise to an inter- or intramolecular charge-transfer complexes, which causes a shift in absorption maximum in the bathochromic sense. The measured spectra are consistent with our assumption.

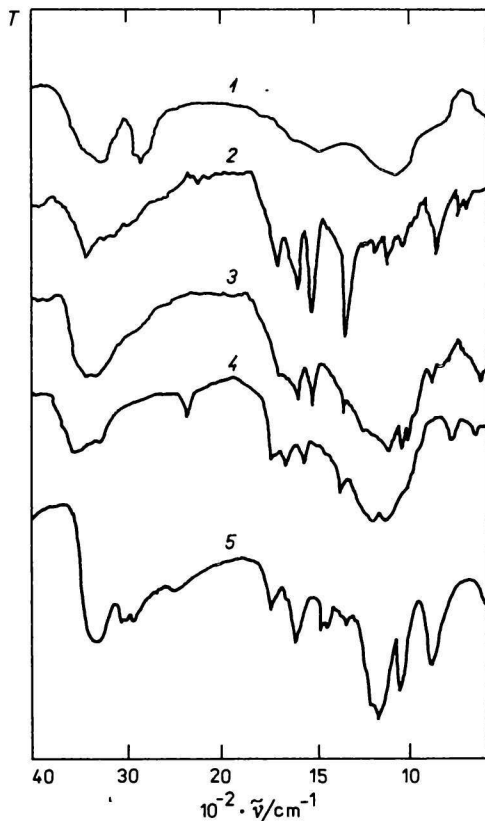
The infrared spectra of the synthesized derivatives are represented in Fig. 3 and described in Table 2. The presence of the absorption bands at $\tilde{\nu}(\nu_{\text{as}}(\text{NO}_2)) = 1510 \text{ cm}^{-1}$ and at $\tilde{\nu}(\nu_{\text{s}}(\text{NO}_2)) = 1345 \text{ cm}^{-1}$ of products *I*, *II*, and *III* documents the fact that the present nitro groups were not subjected to total reduction under the given reaction conditions. A significant change did not appear even if the reaction time was doubled and the content of the reducing agent was increased. Similarly, the degree of substitution of product *II* calculated on the basis of elemental analysis is higher than that one determined by the method of diazotation (Table 1).

As for the amino derivatives, we may observe the accentuated absorption maximum in the $\tilde{\nu}$ region $3300\text{--}3500 \text{ cm}^{-1}$ which corresponds to symmetrical vibrations of the amino group. The bending vibrations of the amino groups in the $\tilde{\nu}$ region $1590\text{--}1610 \text{ cm}^{-1}$ and $650\text{--}900 \text{ cm}^{-1}$ must be attributed to overlapped vibrations of the double bonds of the aromatic ring and amino group. As it results from Fig. 3, further absorption band with the maximum at $\tilde{\nu} = 1690 \text{ cm}^{-1}$ is to be observed for all synthesized derivatives. The presence of this band may be explained by the formation of the carbonyl or carboxyl group owing to a partial oxidative destruction of polymer chain which cannot be excluded with respect to the reaction conditions and acid medium [8].

The results of measurements of resistivity of the investigated derivatives of cellulose are given in Table 1 and Fig. 4. It follows from these results that the

Fig. 3. Infrared spectra of the synthesized derivatives of cellulose.

1. Hydroxyethylcellulose; 2. 4-nitrobenzaldehyde hydroxyethylcellulose acetal (I); 3. 4-aminobenzaldehyde hydroxyethylcellulose acetal (II); 4. (4-diazoniobenzaldehyde chloride) hydroxyethylcellulose acetal (III); 5. 4-*N*-dimethylaminobenzaldehyde hydroxyethylcellulose acetal (IV).



temperature dependence of resistivity is governed by the relationship valid for semiconductors [9, 10]

$$\rho = \rho_0 \exp \left[\frac{\Delta E}{kT} \right]$$

where ΔE is the activation energy of free charge carriers necessary for reaching the conduction band for extrinsic semiconductors or the half-width of the forbidden band for intrinsic semiconductors. The symbols ρ_0 , k , and T stand for the material constant, Boltzmann constant, and absolute temperature, respectively.

A comparison of resistivity of the investigated derivatives of cellulose shows that derivative II which contains both donating and accepting groups has a lower resistivity than the derivatives which contain only a donating or accepting group (I, IV). The difference between the measured resistivities of product I and II is especially significant because its value reaches even six decimal orders.

The values of the resistivity activation energies of the synthesized derivatives are

not too different and their values are equal to 0.42—0.63 eV (Table 1). By mixing product *I* and *IV* in equal mass ratio the resistivity dropped by five decimal orders when compared with the resistivity of product *I*. On the basis of these results, we may conclude that the decrease in resistivity of derivative *II* which contains both donating and accepting groups may be caused by the formation of some intra- or intermolecular charge-transfer complexes which usually exhibit a decreased resistivity when compared with the resistivity of the isolated components constituting the complex [11]. A possible intermolecular interaction is also suggested by the decrease in resistivity of mechanical mixture of products *I* and *IV* as well as by the

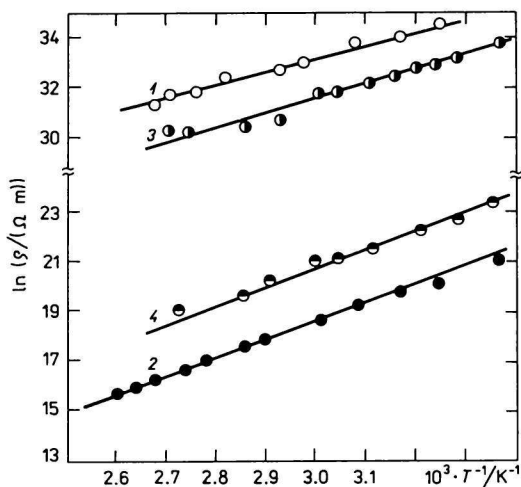


Fig. 4. Variation of resistivity with reciprocal value of temperature.

1. Product *I*; 2. product *II*; 3. product *IV*; 4. mechanical mixture of products *I* and *IV*.

shift in absorption maxima and extension of absorption region in bathochromic sense observed for product *II*.

The influence of the absorbed air humidity was observed for amino derivative *IV*, but not for derivative *II* though it exhibited good solubility in water. As for product *IV*, its resistivity in inert atmosphere was increased by three decimal orders with respect to its resistivity measured in air. This observation indicates the fact that the number of the free OH groups of product *II* able to bind water is limited and the amino group in the aromatic ring takes part in formation of the complex. The replacement of the amino groups by the diazonium salt which has a high affinity to the molecules of water caused the considerable difference between the resistivity measured in air and inert atmosphere. In this case, the difference corresponded even to seven decimal orders. The sample of the

diazonium salt exhibited good stability at laboratory temperature and its thermal decomposition was not observed even after several weeks.

The difference between the measured resistivity also manifested itself for a mechanical mixture of products *I* and *IV* measured in air and inert atmosphere and corresponded to one decimal order when compared with product *I*. This smaller difference may be explained by a higher degree of substitution which was attained for the product with the bonded nitroaryl groups.

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