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Conductivity of molecular semiconductor material based on monomeric and polymeric methacroylacetophenone

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Abstract. The method of impedance spectroscopy was used to study the conductivity of the films of sodium salt of 2-methyl-5-phenylpenten-2-3-5-dione (Namphpd) and polymer based on it that were prepared using drip application from various solvents. It was shown that the use of different solvents when applying films from solutions allows to obtain materials with different types of conductivity due to the specific solvation of the materials.

Keywords: impedance spectroscopy, monomer, polymer, conductivity, organic (molecular) semiconductors, methacroylacetophenone.

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1. Introduction

In recent years, intensive researches performed in the field of semiconductor physics and microelectronics have been aimed at expanding the circle of semiconductor materials with new properties, in particular, at the development of such a field as molecular electronics.

The increased interest in organic semiconductors is associated primarily with relative simplicity of technology and the low cost of the obtained material. Moreover, the use of organic molecules in various configurations opens wide possibilities for modifying both the electrophysical and optical properties of the material.

One of the varieties of semiconductor materials is organic (molecular) semiconductors – wide class of substances related by the type of bond to molecular compounds and possessing noticeable electrical conductivity. These include, for example, molecular crystals, organic dyes, charge-transfer molecular complexes, biological substances (chlorophyll, β-carotene), ion-radical salts, as well as polymers.

An important parameter characterizing the speed of organic semiconductors is the mobility of charge carriers. Now, obtained are organic semiconductors in which this parameter is comparable in its magnitude with the mobility of charge carriers in amorphous silicon (a-Si), but so far, it is much lower than that in polycrystalline silicon (*p*-Si).

The electrical conductivity of organic semiconductors, as a rule, is low ($\sim 10^{-10}$ $\text{Ohm}^{-1}\cdot\text{cm}^{-1}$), and the mobility of charge carriers greatly increases under the action of light (10^3–10^5 $\text{cm}^2/\text{V}\cdot\text{s}$). However, some organic semiconductors (crystals and polymers based on tetracyanquinodimethane (TCNQ) compounds, complexes based on phthalocyanine, perylene, violanthrene, *etc.*) have the electrical conductivity at room temperature comparable with that of classical inorganic semiconductors.

Molecular electronics based on organic semiconductors is an important subject for various researches and development. This trend can be explained by the fact that organic semiconductors seem to be promising material for use as an active layer in optoelectronic devices, namely: field-effect transistors, LEDs, and photocells [1-3]. Materials based on β-diketones, their derivatives, and coordination compounds for these devices are mainly used in the form of thin-film structures from successively deposited layers of the studied materials [4-6].

Deposition of films from various solvents makes it possible to trace the influence of the solvent on the type of conductivity, structure, uniformity, and homogeneity of the obtained film coatings. The study of the electrophysical properties of these materials, in particular, determination of the sign of the main charge carriers in these materials, is actual to identify the features of functioning of the elements of organic electronics, selection of solvent. It should be noted that in recent years, materials that can be used as semiconductors of various types in planar heterostructures (organic electroluminescent materials) have become more widely used [5–9].

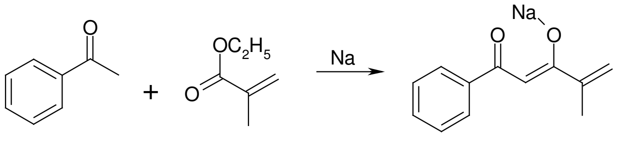
As a rule, the role of conductive materials belongs to organic compounds in particular PEDOT:PSS, PVK, TPD, *etc*. These compounds have only one type of conductivity (*n*- or *p*). Therefore, it becomes actual to synthesize a material that can act as semiconductor of both *n*- and *p*-type conductivity, depending on the solvent of which the films are deposited. Obviously, the influence of the solvent is associated both with the viscosity of the dispersion medium, dielectric conductivity and, of course, with solvation effects or specific solvation. A study of the effect of a solvent on the type of conductivity was not previously carried out.

The aim of this work was to study the conductivity of the films of the sodium salt of 2-methyl-5-phenylpenten-2-3-5-dione (Namphpd) and the polymer based on it, obtained by drip application from various solvents.

2. Experimental technique

2.1. Synthesis of 2-methyl-5-phenyl-penten-1-dione-3,5

The synthesis of 2-methyl-5-phenyl-pentene-1-dione-3.5 was carried out by condensation of acetophenone and ethyl ether of methacrylic acid according to Kleisen [10]. Into the three-necked reactor equipped with a stirrer, reflux condenser and dropping funnel, where 0.5 mol of sodium metal (11.5 g) and 300 cm^3 of dry diethyl ether were placed, a solution of acetophenone 0.5 mol (59 cm^3) and ethyl ether of methacrylic acid 0.5 mol (63 cm^3) was spilled drop, this solution was pre-chilled with a mixture of ice and salt. The reaction mixture was heated, and a yellow precipitate was formed:

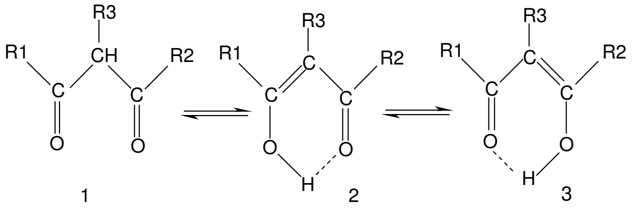


After the last portion of the reagents was introduced, the solution was stirred for 3 hours and left at ~20 °C for 12 hours. After that, the precipitate was filtered off, washed and dried in a dessicator over P_2O_5. The yield of the final product was 76 g (~ 72%). The sodium salt of $C_{12}H_{11}O_2Na$ prepared according to the described procedure is an amorphous yellow powder with melting temperature 216 °C.

The ligand was polymerized at 800 °C in dimethylformamide at the concentration 0.03 mol/L and the initiator concentration of 2,2'-azo-bis (isobutyronitrile) – 0.0003 mol/L in a thermostat for 4 hours. The obtained metal polymer was precipitated from the solution with isopropanol-2.

The purity of the synthesized unsaturated β-diketone was determined by elemental analysis and NMR ^{1}H method (Table).

The position of the CH_3 proton signals differs by ~ 0.2 ppm, which indicates the presence of equilibrium between the ketone and enol forms in the solution:



$R_1 = –C(CH_3) = CH_2$; $R_2 = –C_6H_5$ (for Hmphpd)

The exchange between the ketone and enol forms is rather slow – the exchange rate is less than the band width at half maximum (0.5 Hz). The shift of the signal of OH protons to a weak field indicates formation of an intramolecular hydrogen bond in enol. In addition, a very wide OH signal against the background of fairly narrow signals of protons of CH, CH_2, and CH_3 groups may indicate the presence of several potential wells in which OH-proton can be located. A probable reason for this fact is the competition of intra- and intermolecular hydrogen bonding of enol.

For deposition onto glasses, the samples were dissolved in chloroform ($CHCl_3$), dimethylformamide (DMFA, $N(CH_3)_2CHO$) and alcohol (C_2H_5OH). The concentration of the sample was 0.03 M. On a pre-cleaned glasses with the deposited layer of contact (Ga:In = 50:50 wt.%), a concentrated solution of the substance was spilled drop and left to dry completely.

Table. Elemental analysis and NMR ^{1}H data for unsaturated β-diketones.

Compound	Element, calculated (determined), %			NMR $^1\underline{\mathbf{H}}$ ($CDCl_3$), δ (ppm)
	C	H	Na	
$C_{12}H_{11}O_2Na$	68.55 (68.31)	5.28 (5.20)	10.82 (10.94)	0.97–1.15 (mult., 2H, C–C$\underline{\mathbf{H}}_2$–); 1.98 (single, 3H, C$\underline{\mathbf{H}}_3$); 3.55–3.62 (single, 1H, =C$\underline{\mathbf{H}}$–); 7.05–7.96 (mult. ext., 5H, $\underline{\mathbf{Ph}}$), 16.08 (single wide, 4H, O$\underline{\mathbf{H}}$)

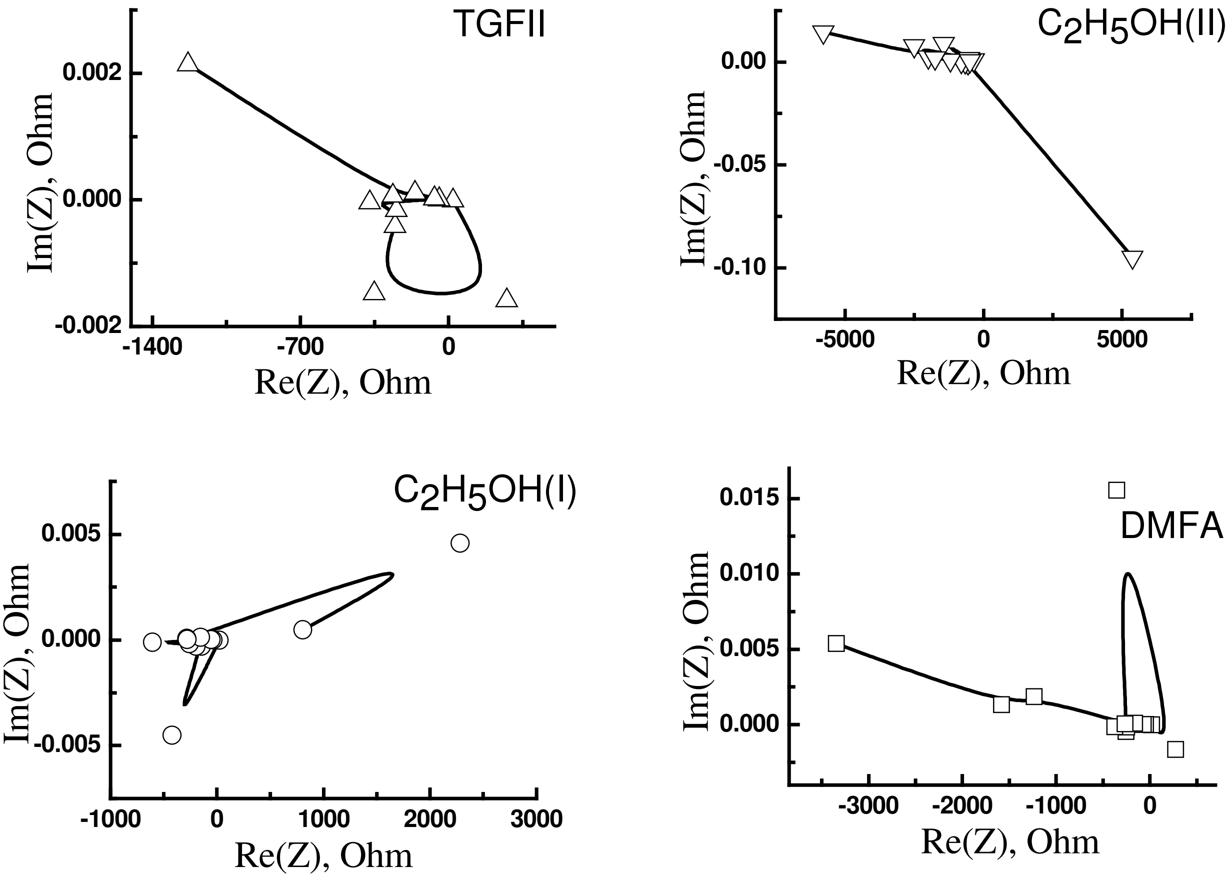


Fig. 1. Nyquist diagrams of the samples.

2.2. Impedance spectroscopy technique

To perform electrophysical studies, the impedance spectrometry technique was used. The impedance characteristics of the samples were determined using "LCR-819"-meter in the range 1…100 kHz with the sinusoidal signal amplitude close to 120 mV. From the technical viewpoint, this method consists of measuring the frequency dependences of the real ($Z'(\omega)$) and imaginary ($Z''(\omega)$) components of the complex impedance inherent to the material under study. As a rule, the obtained frequency characteristics ($Z'(\omega)$ and $Z''(\omega)$) are approximated using an equivalent electric circuit, by selecting its active and reactive elements – R, L, C. For a material homogeneous in its physical properties, the hodograph, as a rule, has the shape of a semicircle with a diameter R and center on the z-axis passing through the origin, which corresponds to the equivalent electrical circuit of a parallel RC circuit.

3. Experimental results and discussion

The impedance hodograph in the coordinates (Z'', Z') in the shape of Nyquist diagrams is shown in Fig. 1.

From the mentioned above, the choice of an equivalent electrical circuit (R, L, C) should be based on the presence of certain physical properties. In our case, the interpretation of the obtained hodographs (Fig. 1) is ambiguous in consequence of the uncertainty in the choice of the dominant technological process of preparing the samples and reflects rather the polarizability of the synthesized medium.

This behavior at low frequencies 10…10^2 Hz indicates a characteristic process of charge transfer in the obtained films, which is associated with ion migration. Some analogy can be drawn with ion-migration polarization that is inherent to dielectrics. It can be assumed that for our case, the synthesized films will have various types of conductivity [13], which is caused by specific solvation. As you know, the influence of a solvent on the electrical conductivity primarily consists in the influence of its viscosity, dielectric function and specific interaction with ions (specific solvation).

The viscosity forces of the solvent inhibit motion of ions. The dielectric properties of the medium affect the effective strength of electric field and interionic potential. The latter values effect not only the velocity of ions, but also the attraction between contralateral ions and,

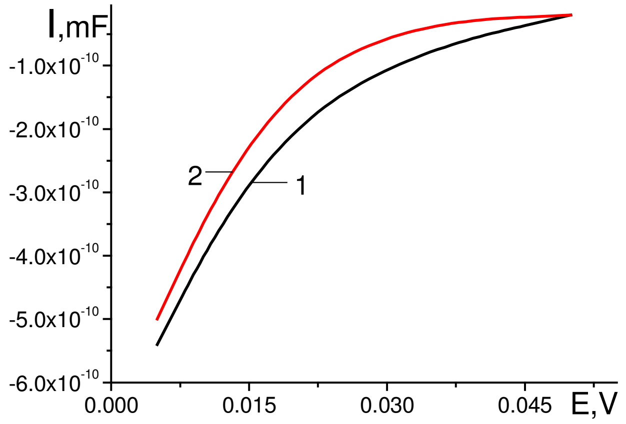


Fig. 2. Voltage-capacitance characteristics of monomer (1) and polymer (2) in C_2H_5OH.

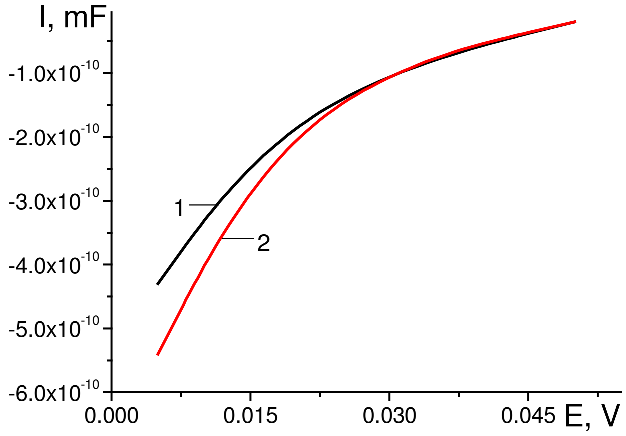


Fig. 3. Voltage-capacitance characteristics of the polymer in DMFA (1) and monomer in C_2H_5OH (2).

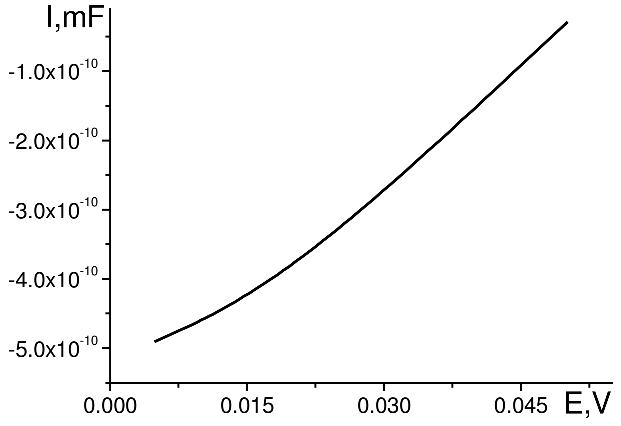


Fig. 4. Voltage-capacitance characteristic of $CHCl_3$ polymer.

therefore, the degree of their binding in pairs. Specific solvation of ions can effect both mobility and association. Solvate shells reduce the tendency of ions to associate. If there are no solvate shells, interaction between ions is enhanced. If the solvent molecule forms associates with the studied compounds, then it is under the influence of powerful electrostatic fields.

Therefore, in this work it will be correct to consider the voltage-capacitance characteristics of the studied objects. Interpretation of the measured voltage-capacitance characteristics of all the samples was carried out (Figs. 2 to 4). The type of conductivity of the studied molecular semiconductor material was determined by the shape of dependence. Being based on the nature of the obtained dependences, we can distinguish three dependences indicating *p*-type conductivity (Figs. 2 and 3) and one dependence – *n*-type (Fig. 4), respectively [11].

The studies of monomeric and polymeric sodium methacroylacetophenate have shown that the same type of conductivity occurs in donor solvents, both proton and aproton ones. As can be seen from Fig. 2, the voltage-capacitance characteristics of the monomer and polymer in ethanol are close, although a significant difference in the shape and slope angle of the curve is noticeable, which may be caused by both lower solubility and, consequently, lower concentration of the initial polymer, and better polymer conductivity as compared with the monomer.

From the analysis of Fig. 3 (monomer film prepared from alcohol and polymer film prepared from DMFA), it is seen that the character (type, bending) of the curve is exactly the same, which may indicate the same solvation (type of solvation) of these compounds. Obviously, there is a certain dependence on the concentration, so, the solubility of monomer is better in alcohol and the solubility of polymer in DMFA, which may indicate a slight difference in the concentration and dispersion of the obtained systems. The shape and size of particles significantly influence physical characteristics of objects. Since these films are two-dimensional nanoparticles (only one size is in the nanometer range), it is probable that the electrophysical properties also depend on which group of objects they belong to: regular or irregular [14]. Despite the different nature of the solvents, as a rule, alcohol is an electrophilic agent, but it is known that in some cases it behaves like a nucleophile.

In the case of a film obtained from chloroform (Fig. 4), the angle of inclination, shape of the curve are similar to the films of DMFA and alcohol, only bending in the opposite direction, which is probably caused by a similar concentration of polymers in the film and indicates the same electron mobility. Of all the used solvents, chloroform ($CHCl_3$) is the least polar electrophilic agent. If we compare the dielectric functions of chloroform $CHCl_3$ and DMFA, then it is 7.5 times less than that in DMF and 5 times lower than that in alcohol, which, of course, affects also the mechanism of solvation [15-18]. Depending on the nature of the solvent, the type of conductivity of the films changes, which is caused by a different mechanism of solvation, so, in the case of the nucleophilic mechanism of solvation (DMFA, alcohol), we have *p*-type of conductivity, and in the case of electrophilic (chloroform) – *n*-type.

For known values of the dielectric function inherent to solvents and chemical components ($\varepsilon = 4\ldots40$ [12]), the concentration in the depletion region N_f and barrier capacitance C_s are related by the simple expression $N_f = (C_s/S)^2(4k_\mathrm{B}T)/(\varepsilon\varepsilon_0 e^2)$, where k_B is the Boltzmann constant, $T = 300$ K, ε – dielectric function of materials (films), ε_0 – vacuum electric constant; *e* – electron charge, $S = 0.01\ \mathrm{m}^2$ – area of the sample. Molecular semiconductor films are characterized by the value of N_f that varies within the range $4.7\ 10^{12}\ldots4.7\ 10^{11}\ \mathrm{m}^{-2}$. Obviously, the value of N_f reflects the fixed charge of the semiconductor material based on monomeric and polymeric methacroylacetophenone that is under studying.

4. Conclusions

Thus, the studies have shown that the use of various solvents in the deposition of films from solutions of the monomer and polymer compounds allows to obtain materials with various types of conductivity, which is caused by specific solvation of these materials.

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