PHOTOCONDUCTIVITY OF POLYMERIC LAYERS WITH DIAZONY SALTS

It has been performed the experimental and theoretical (with using the quantum-chemical calculation methods: methods MNDO/d and AM1) studying the photoelectric properties of the polymeric layers with diazony salts (SD). In particular, it is studied the hole photoconductivity in the matrix, the photocurrent kinetics for different concentrations of the studied diazony salts in the polymer matrix, other photoelectric properties.

1. Introduction

To present time there are carried out numerous experimental and theoretical works data showing that the excitation relaxation processes in polymeric materials with different complex salts do not prevent leakage of important science and practice processes in the highly excited states such as generation of carriers, photochemical and radiation-chemical processes. For example, studying a photoconductivity of the polyacene linear crystals (anthracene, tetracene, pentatens) [2] showed that its high quantum efficiency is observed only under irradiation of the highly excited molecules when there is possible a birth of holes and free electrons. During the process of relaxation from the highly excited state a molecule can stay at an intermediate state corresponding to electron transfer between the molecule and the crystal. Let us remind that the processes of charge separation in the non-equilibrium relaxation of highly excited state are theoretically considered already in the works by Onsager [3].

We have earlier found that light-sensitive components are able to provide the reaction phototransfer electron of these components in the matrix and vice versa. Only diazonium salts (SD) (photosensitive components of diazonium type materials) provide only one-way process - from the matrix to the diazonium cation [2-6].

The second reason for the use of diazonium salts is the fact that they have CN bond, which is characteristic of type Xe-O. As result, the SD has a high photochemical activity. This type of bond is present in the excited molecules of resazurin (NO-bond), on which it was found photochemical activity in the rezazuryne.

In this paper we present the results of experimental and theoretical studying the photoelectric properties of a system “polymer – SD”. As binding polymer we have taken the polyvinyl alcohol (PVA) (I), polyvinyl-pyrrolidone (PVP) (II), poliviniletylal (PVE) (III) and polyvinyl acetate (PVA) (IV). Diazocomponents were choosen as the tetrafluoroboraties of the para-dietylamino-fenildiazonium (DEAFD) and para-metokxy-fenildiazonium (MFD). Device for measuring photovoltaic properties of polymer layers described in Refs. [2-4]. It is worth mentioning that in the manufacture of plastic layers from solution on a horizontal quartz surface they are heterogeneous in thickness: about denser layers of the substrate and on the free surface loosened. Therefore, we can find only the average parameters describing photoconductivity of polymer layers.

2. Quantum-chemical studying

For the theoretical description of the experimental data we used methods of formal kinetics of photoprocesses in layers and known quantum-chemical methods of research (the method of mo-
lecular dynamics MM +, based on the method MM2 [2] and semi-empirical methods such as MNDO/d and AM1 [6-15].

For elucidation of the mechanism of electron transfer in the system matrix, we performed the MD calculations of energy in such a system without electron transfer, with transfer from the matrix to SD and vice versa, calculations of the energy structure of the SD in the undissociated and dissociated states, an electron phototransfer excitation spectrum.

Besides, we studied the opportunities of the electron dark transfer electrons in the system “matrix – photoproducts”, formed by dissociation diazonium cation. The calculation results are presented in Tables 1 and 2.

**Table 1.**

Ionization potential (IG) and energy affinity (EA) to electron matrix molecules and SD (in brackets - in the ground state).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>I₇ EB</th>
<th>E₈ EB</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVE</td>
<td>10,44</td>
<td>-3,03</td>
</tr>
<tr>
<td>PVP</td>
<td>8,72</td>
<td>-3,54</td>
</tr>
<tr>
<td>PVA</td>
<td>10,93</td>
<td>-0,61</td>
</tr>
<tr>
<td>PVS</td>
<td>10,67</td>
<td>-2,59</td>
</tr>
<tr>
<td>MFD∙BF₄</td>
<td>10,48</td>
<td>3,15</td>
</tr>
<tr>
<td>DEAFD∙BF₄</td>
<td>9,30</td>
<td>2,88</td>
</tr>
<tr>
<td>MFD</td>
<td>12,97</td>
<td>6,65 (10,61)</td>
</tr>
<tr>
<td>DEAFD</td>
<td>12,04</td>
<td>6,26 (9,52)</td>
</tr>
</tbody>
</table>

In table 2 we list the data on the energy required for charge transfer. These data do not take into account the Coulomb interaction between the charges after the charge transfer process. After the charge transfer, the geometric structure of the system turns non-optimized. Optimization significantly reduces the energy system. It should be emphasized that this reduction exceeds the energy of the Coulomb interaction between the charges after charge transfer. Thus, the geometric optimization of molecular system influences on the distance of the holes and an appearance of photocurrent (photovoltage). As a result, we will see hole photovoltaic conductivity in the matrix. The positions of the wavelength absorption band in the MFD - 3,96 eV, and DEAFD - 3,26 eV.

According to Table . V.2 in PvE is generation at E> 4,19 eV (MFA) and E> 4,43 eV (DEAFD). Similarly, in PVA - 4,35 and 4,60 eV, in PVP - 3,96 and 4,20 eV.

**Table 2.**

The energy required for electron transfer (T) from the matrix (M) on SD and from the SD on the matrix.

<table>
<thead>
<tr>
<th>T on SD</th>
<th>T on M</th>
<th>Condition</th>
<th>Eₜ</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>7,30</td>
<td>13,51</td>
<td>nopt</td>
<td></td>
<td>PVE + MFD∙BF₄</td>
</tr>
<tr>
<td>4,19</td>
<td>10,85</td>
<td>opt</td>
<td>3,11</td>
<td></td>
</tr>
<tr>
<td>7,55</td>
<td>12,32</td>
<td>nopt</td>
<td></td>
<td>PVE + DEAFD∙BF₄</td>
</tr>
<tr>
<td>4,43</td>
<td>9,81</td>
<td>opt</td>
<td>3,12</td>
<td></td>
</tr>
<tr>
<td>5,73</td>
<td>13,99</td>
<td>nopt</td>
<td></td>
<td>PVP + MFD∙BF₄</td>
</tr>
<tr>
<td>3,97</td>
<td>10,22</td>
<td>opt</td>
<td>1,76</td>
<td></td>
</tr>
<tr>
<td>5,32</td>
<td>12,84</td>
<td>nopt</td>
<td></td>
<td>PVP + DEAFD∙BF₄</td>
</tr>
<tr>
<td>4,24</td>
<td>9,22</td>
<td>opt</td>
<td>1,77</td>
<td></td>
</tr>
<tr>
<td>7,78</td>
<td>11,09</td>
<td>nopt</td>
<td></td>
<td>PVA + MFD∙BF₄</td>
</tr>
<tr>
<td>4,35</td>
<td>9,95</td>
<td>opt</td>
<td>3,44</td>
<td></td>
</tr>
<tr>
<td>8,04</td>
<td>9,91</td>
<td>nopt</td>
<td></td>
<td>PVA + DEAFD∙BF₄</td>
</tr>
<tr>
<td>4,60</td>
<td>8,92</td>
<td>opt</td>
<td>3,45</td>
<td></td>
</tr>
</tbody>
</table>

Note: nopt – is corresponding to the electron transfer without changing the geometry of molecules (Kramers-Kronih process), opt - after optimizing the geometry.

Thus, the use of the MFD provide a photoconductivity in the PVP during excitation in the long-wavelength absorption band. In a case of the other polymers or using DEAFD it would be necessary excitation into higher states.

The SD photolysis leads to the formation of the aryl cation. It is important to know whether processes involving these cations may cause the phenomenon of photoconductivity. We calculated the energy balance for different transformations of the aryl cation. It turned out that the metoksyfenil cations in the dark conditions can capture an electron from the matrix, leading to hole conductivity.
At the same time the diethylaminofenil cations can not capture electrons (threshold value within 1.2 ÷ 1.6 eV).

Calculation has showed that both types of aryl cations can drag the hydrogen atom from the macromolecule. In addition, both aryl cations readily react with the anion, resulting in formation of two neutral molecules. Thus, this reaction does not give a contribution to photoconductivity. However, it appears that in the presence of water vapor it is possible formation of the phenols and acid in the presence of water vapor

\[ (H_2O + H^+ BF_4^- \rightarrow H_3O^+ + BF_4^-) \]

and it can give a contribution to the slow component of photoconductivity.

3. Experimental results and discussion

In Figure 1 we present the photocurrent kinetics for different concentrations of the studied SD in the PVA matrix during the excitation switching on and off. From the figure it is clear that the current increasing stops in over time \( t \). So we can assume that all carriers have reached the opposite electrode and there is a dynamic equilibrium. In this case current increasing stops.

![Figure 1. The photocurrent kinetics for different concentrations of the studied SD in the PVA matrix during the excitation switching on and off.](image)

Using data on photoconductivity of polymer layers, we calculated the average values of the concentration of the charge carriers (generated by light) \( n \) upon the concentration of the molecules SD (Fig. 2). These values show that the introduction of SD into the PVA and PVP increases concentration of \( n \), however introduction of the SD into the PVE reduces it. As for the PVA matrix, its reaction to the introduction of the MFD and DEAFD diametrically opposite. Really, the DEAFD increases value \( n \) and MDF decreases its value.

The defective or uncontrolled impurities can be by reson of the above said fact. In fact, they provide adequate electrical conductivity. When one adds the low concentrations of the SD it is possible removing the defects and consequently reducing the photocurrent.

![Figure 2. The dependence of the carrier concentration upon the concentration of SD in layers: a - MFD; b - DEAFD.](image)
From the data of the EPR spectroscopy at low temperatures (77 K) [5] and the results of photochemical studies at the room temperature [5,62] it is known that the quantum phototransfer yield of an electron on the MFD is more than on the DEAFD, i.e. its energy levels are lying lower than in DEAFD. Thus, the electron is much easier to go from the matrix on the MFD in comparison with the DEAFD. This conclusion is confirmed by the results of quantum-chemical calculations are presented in Table 1.

Availability photontransfer electron in the system “SD-matrix” according to the reaction:

$$\text{SD} + \text{M} \xrightarrow{h\nu} \text{SD}^- + \text{M}^+$$

can be determined by evaluating the heat of reaction:

$$Q = I_M - E_A^{G} - h\nu - E_C.$$

If this value is less than zero, the electron transfer reaction proceeds exothermically. Otherwise it is endothermic.

Since the SD is dissociated into ions in polymer matrix, then the SD affinity energy to electron is reduced by more than 3 eV. Substituting the data of Table 1 in the formula for calculating the value of Q, we find that DEAFD •BF$_4^-$ in the lower excited state may take one electron from the PVP ($Q = -0.1$ eV).

For other matrices, this value is greater than 1 eV. Thus, electron transfer is possible only when excited into higher energy states or from impurities in the polymer matrix.

In the case of the MFD•BF$_4^-$ electron transfer is possible from all matrices on SD. The value of Q is -1.05 eV in PVP and does not exceed 0.3 eV in other matrices (heat and electric field are able to overcome such barriers). Thus, the largest energy barrier exists between the lower free energy state of the excited cation DEAFD and top employed state of the PVS and PVA matrices. The value of the photocurrent in these cases should be minimal, that is observed experimentally. However, the integral absorption of MFD is less than DEAFD. This leads to the fact that value of the photocurrent in the PVA with the MFD is almost two times lower than with DEAFD.

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References


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Abstract

It has been performed the experimental and theoretical (with using the quantum-chemical calculation methods: methods MNDO/d and AM1) studying the photoelectric properties of the polymeric layers with diazonium salts. In particular, it is studied the hole photoconductivity in the matrix, the photocurrent kinetics for different concentrations of the studied diazonium salts in the polymer matrix, other photoelectric properties.

Key words: polymer layers with diazonium salts, photoelectric properties

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ФОТОПРОВОДИМОСТЬ ПОЛИМЕРНЫХ СЛОЕВ С СОЛЯМИ ДИАЗОНИЯ

Резюме

Проведено экспериментальное и теоретическое (с помощью квантово-химических методов расчета типа методов MNDO/d, AM1) изучение фотоэлектрических свойств полимерных слоев с солями диазония. В частности, изучена дырочная фотопроводимость в матрице, кинетика фототока для различных концентраций рассмотренных солей диазония в полимерной матрице, другие фотоэлектрические свойства.

Ключевые слова: полимерные слои с солями диазония, фотоэлектрические свойства
ФОТОПРОВІДНІСТЬ ПОЛІМЕРНИХ ШАРІВ З СОЛЯМИ ДІАЗОНІЮ

Резюме
Проведене експериментальне і теоретичне (за допомогою квантово-хімічних методів розрахунку: типу методів MNDO/d, AM1) вивчення фотоелектричних властивостей полімерних шарів з солями діазонію. Зокрема, вивчена дирочна фотопроводимість в матриці, кінетика фотоструму для різних концентрацій розглянутих солей діазонію в полімерній матриці, інші фотоелектричні властивості.

Ключові слова: полімерних шарів з солями діазонію, фотоелектричні властивості