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Poly(3,4-ethylenedioxythiophene):Synthesis and Properties

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Abstract: **The high concentration emulsion polymerization of 3,4-ethylenedioxythiophene in the presence of sodium salt of 2-naphthalenesulfonic acid as dopant and emulsifier and ferrum(III) sulfate as oxidant is described. By means of IR-spectroscopy it was shown that the resulting polymer is poly(3,4-ethylenedioxythiophene) and by means of transmittance electron microscopy it was demonstrated that it is characterized by the morphology of shapeless flat formations. It was found out that the conductivity of poly(3,4-ethylenedioxythiophene) obtained by this method depends on the amount of washing water passing through the maximal conductivity value 160 S/cm. The influence of heat treatment at 125°C of poly(3,4-ethylenedioxythiophene on its conductivity and morphology was studied. It was shown that the initial conductivity of poly(3,4-ethylenedioxythiophene) considerably influences the conductivity of the heat treated poly(3,4-ethylenedioxythiophene). The heating of poly(3,4-ethylenedioxythiophene) with low conductivity leads to the decrease of its conductivity while the heating of the poly(3,4-ethylenedioxythiophene) with maximal conductivity of 160 S/cm leads to increase of its conductivity up to several thousands S/cm. Transmittance electron microscopy shows that the morphology of poly(3,4-ethylenedioxythiophene) with conductivity of several S/cm are monocrystalls.**

Keywords: **conducting polymers, PEDOT, emulsion polymerization, conductivity, monocrystals**

I INTRODUCTION

Polythiophene and its derivatives have been at the center of considerable scientific interest for their attractive and superior chemical and physical properties [1]. Among the derivatives of polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT), is one of the most successful conducting polymers because of its low bandgap, excellent environmental stability, high electrical conductivity, and transparency in thin oxidized films. Since PEDOT was first synthesized in 1989, many studies on PEDOT have been carried out. Many applications have been reported for solid electrolytic capacitors, antielectrostatic agents, transparent electrodes in light emitting diodes, and underlayers for the metallization of printed circuit boards.

Numerous researches have been made on the syntheses of PEDOT by the electrochemical and chemical oxidative polymerizations and organic synthesis of 3,4-ethylenedioxythiophene (EDOT) [2-4]. The latter has been recognized as more suitable for mass production.

Only several years ago a new technique of polythiophene synthesis was suggested by Japanese scientists [5]. It is performed by high-concentration emulsion polymerization of ethylenedioxythiophene (EDOT) in the presence of sodium salt of 2-naphthalenesulfonic acid (2-NaNS) as dopant and ferrous sulfate as oxidant. The conductivity of obtained by this method PEDOT was 160 S/cm. In present article we developed a route for the increase of PEDOT conductivity from 100 S/cm to several thousands.

II EXPERIMENTAL

3,4-ethylenedioxythiophene was purchased from Aldrich, sodium salt of 2-naphthalenesulfonic acid was purchased from Fluka and $Fe_2(SO_4)_3$ was purchased from Reachim (Russia) and used without further purification. Bidistilled water was used.

The structure of PEDOT was analyzed by using both a small-angle X-ray (SAX, 45 kV, 25 mA; URS-60, Russia) and wide-angle X-ray (WAX, 40 kV, 30 mA; URS-55, Russia). Ni-filtered Cu $K_{\alpha 2}$ radiation was used. Electrical conductivities of PEDOT pellets were measured employing the usual four-probe method using a Loresta-GP MCP-T610 conductivity meter (Mitsubishi Chem. Corporation, Japan). To examine the morphology of the PEDOT transmittance electronic microscopy (TEM) LEO912 AB OMEGA was used.

Water suspension of sodium salt of 2-NaNS (2.286 g in 10 ml H_2O) is mixed with 3,4-ethylenedioxythiophene (EDOT, 1 ml) on a magnet stirrer. The water solution of $Fe_2(SO_4)_3$ x H_2O (3.276.g.in 5 ml H_2O) is added drop-wise by stirring to the suspension. The reaction mixture is stirred during 9 hours at room temperature.

The obtained black deposition – the polymerization product - is collected by centrifugation with centrifuge Micro 12-25 (Hettich Zentrifugen, Germany), ω = 15000 rpm, washed by acetone (twice per 12 ml) and dried on air during the whole night. PEDOT was separated from the reaction mixture by centrifugation. PEDOT powder is pressed into tablets with 10 mm in diameter on a hydraulic press at the pressure of 15 MPa. The thickness of the tablets is measured with a micrometer MKC-25 from “Ethalon” (Russia).

III RESULTS AND DISCUSSION

Emulsion polymerization of EDOT in the presence of 2-NaNS and $Fe_2(SO_4)_3$ contains several steps [5]. First step includes the mixing of EDOT, 2-NaNS and ferrum(III) sulfate in water emulsion during 10 hours at room temperature followed with resulting PEDOT isolation. The conductivity of thus obtained PEDOT was found to be 1-2 S/cm.

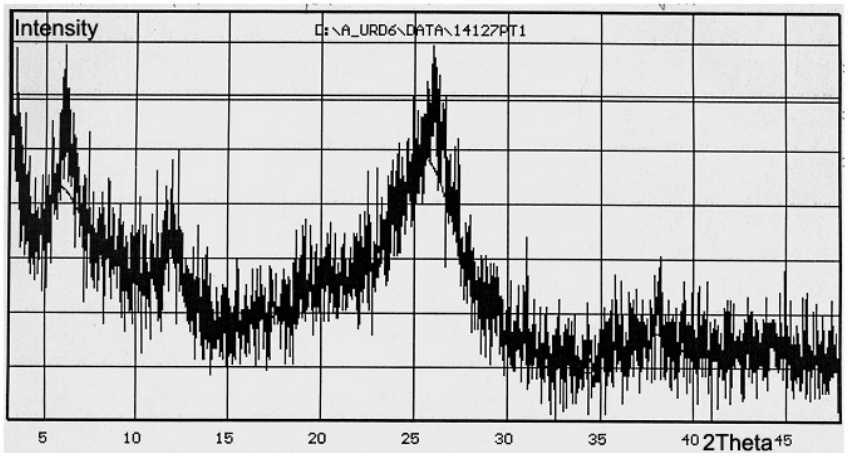

Fig. 1. Diffraction pattern of PEDOT with conductivity 160 S/cm

FT-IR spectrum of synthesized polymer shows the peaks at 1525 and 1330 cm^{-1} (C–C and/or C=C stretchings of the thiophene ring), 1197 cm^{-1} (originated from the C-O-C bond), 991, 850 and 690 cm^{-1} (ν(C-S) and δ(C-H)) [6]. Thus one can conclude that emulsion polymerization product is PEDOT.

In order to characterize PEDOT structure we studied it by X-ray (Fig. 1).The diffraction pattern shows 3 main reflections which are correspond to the interplanar spacings d = 14.7, 7.3 and 3.4 Å which are almost the same as characteristic for PEDOT obtained by Lei Y. et al. [5]. It was proposed that PEDOT structure contains the package of sheets, in each of them PEDOT chains are located parallel to each other with doping agents between them.

The second step of the emulsion polymerization of EDOT in the presence of 2-NaNS and $Fe_2(SO_4)_3$ includes the washing of isolated PEDOT with different portions of water following with conductivity measurement. Fig. 2 shows the dependence of PEDOT conductivity on the amount of washing water.

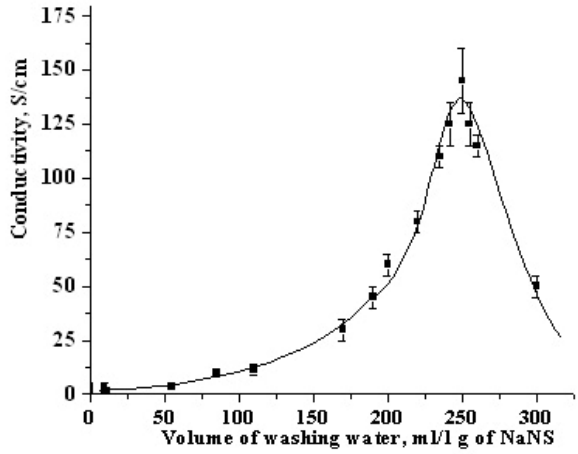

Fig. 2. The dependence of electric conductivity of the product washed on the distilled water

One can see that the increase of washing water amount leads to the increase of conductivity from 1 S/cm to approx. 160 S/cm followed with the decrease of conductivity. Such behavior can be explained in the following way. On the first step of the conductivity increase we washed off the excess amount of 2-NaNS and on the second step of the conductivity decrease we begin to wash off 2-NaNS which dopes PEDOT transferring it to the less conductive state.

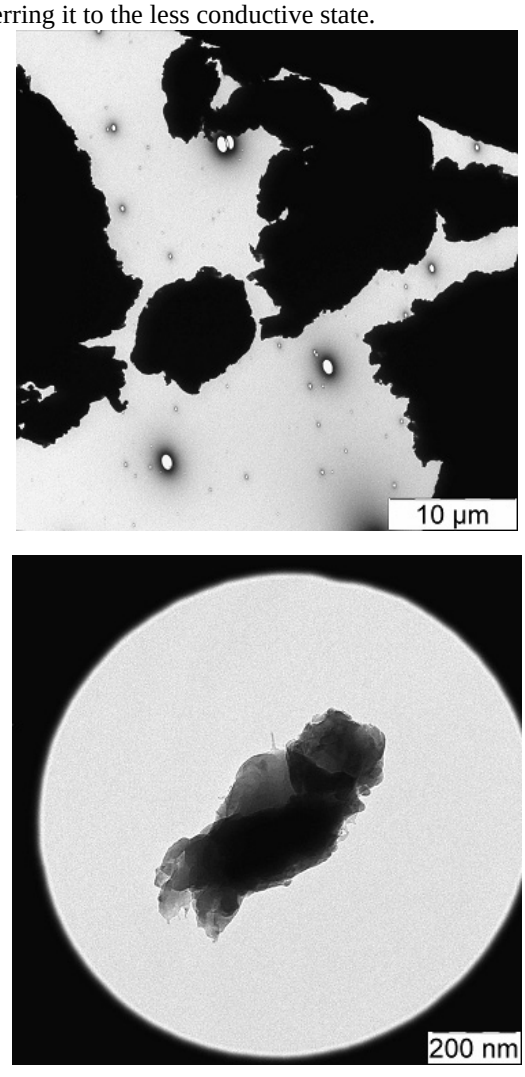

Fig. 3. TEM-images of PEDOT with conductivity 160 S/cm

TEM-images of PEDOT with conductivity 100-150 S/cm show shapeless flat formations.

In order to increase PEDOT conductivity we propose that heating of it can lead to postpolymerization of PEDOT with the formation of more regular structure. Thus we have prepared 3 samples of PEDOT: (1) as synthesized PEDOT with conductivity of several S/cm, (2) PEDOT washed till maximal conductivity (160 S/cm) and (3) over washed PEDOT with conductivity 50 S/cm. All of them were heated at 125°C and the conductivity was measured during different time intervals (Fig. 4).

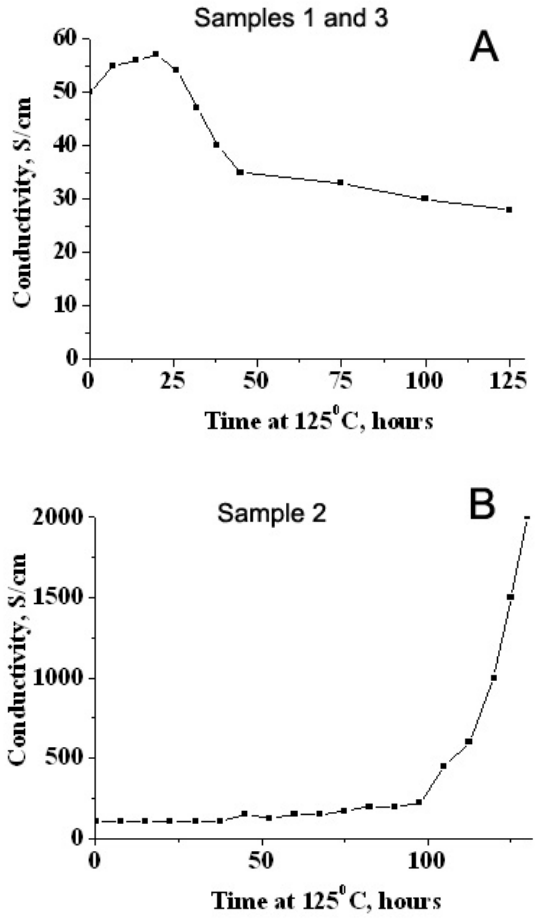

Fig. 4. Dependence of PEDOT conductivity on heating at 125°C time for (A): samples 1 and 3 and (B) Sample 2

Fig. 4A shows that for samples 1 and 3 the increase of heat treatment time in the beginning leads to the small increase of conductivity, while the further increase leads to the decrease of conductivity approximately 2 times. However the main important result was obtained for sample 2 with initial conductivity about 150 S/cm. As one can see on Fig. 4b the first increase of heat treatment time up to 100 hours doesn't lead to any changes in conductivity. However, further increase of heat treatment time during more than 100 hours leads to considerable increase of conductivity up to 2000 S/cm or higher. However after grinding of the pellet with conductivity 2000 S/cm and pressing again in pellet the conductivity was found to be only 50 S/cm. This may be explained by the destroying of regular packing formed during heating of the pressed pellet. In order to confirm this suggestion we have studied the morphology of PEDOT with conductivity of 2000 S/cm (Fig. 5).

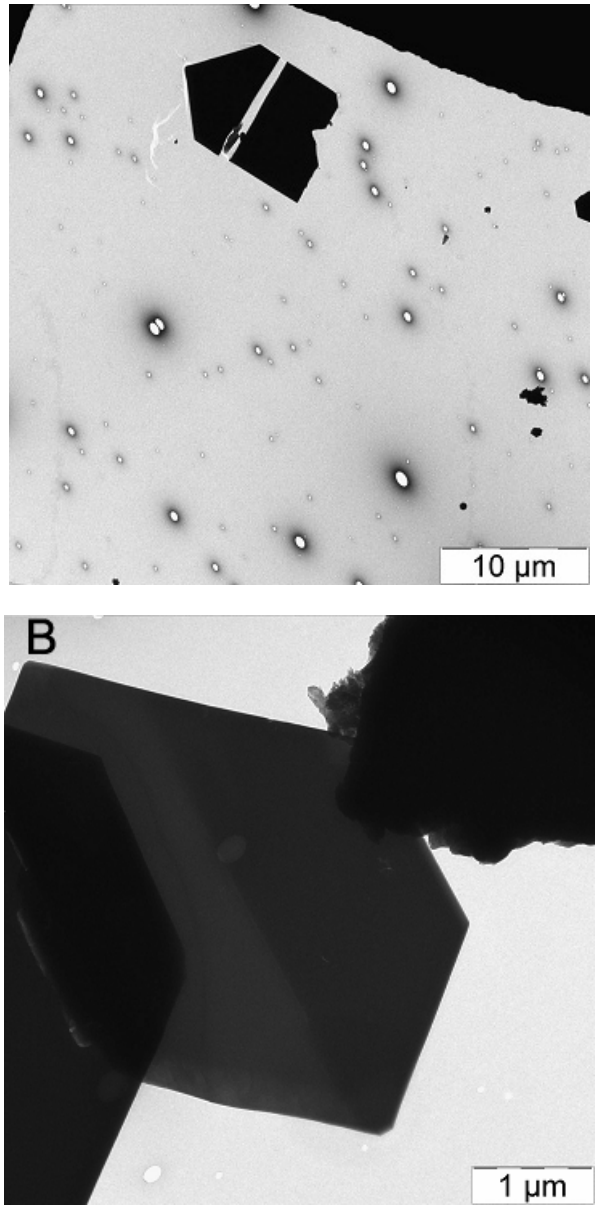

Fig. 5. TEM-images of PEDOT with conductivity 2000 S/cm

One can see that heat treatment leads to formation of right-shaped PEDOT monocrystalls. Thus the increase in conductivity up to 2000 S/cm and more can be attributed to the fact that the heated mixture contains the salt of 2-naphthalene sulfonic acid and iron (II), which by heating is exposed to desulfonation, forming naphthalene. Naphthalene melts, and that promotes the PEDOT crystallization and the formation of highly regular structures. At long-term heating naphthalene is removed from the system due to sublimation. According to IR-spectra, the heated samples mainly contain doped PEDOT and minor amount of ferric sulfate (II).

IV CONCLUSION

Thus we can conclude that new, cheap and simple synthesis of PEDOT with conductivity of several thousands S/cm is

suggested. This method includes: high-concentrated emulsion polymerization of EDOT in the presence of emulsifier and oxidant; washing of the synthesized PEDOT leading to the increase of conductivity from 1 to approx. 150 S/cm and heating the washed PEDOT at 125°C during more than 100 hours.

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Olga Pyshkina, Aleksejs Kubarkov, Vladimirs Sergeyevs. Poli(3,4-etilēndioksitiofēns): sintēze un īpašības.
Aprakstīta 3,4-etilēndioksitiofēna augstas koncentrācijas emulsijas polimerizācija 2-naftalēnsulfonskābes nātrija sāls kā dopanta un emulgatora un dzelzs(III)sulfāta kā oksidanta klātbūtnē. Ar infrasarkanās spektroskopijas metodi parādīja, ka iegūtais polimērs ir poli(3,4-etilēndioksitiofēns) un ar transmisijas elektronmikroskopijas metodi parādīja, ka to raksturo neizteiktas formas plakanu veidojumu morfoloģija. Parādīts, ka pēc šīs metodes iegūtā poli(3,4-etilēndioksitiofēna) vadītspējas maksimālā vērtība ir 160 S/cm un tā ir atkarīga no mazgājamā ūdens daudzuma. Pētīta arī poli(3,4-etilēndioksitiofēna) termiskās apstrādes pie 125^{o}C ietekme uz tā morfoloģiju un vadītspēju. Parādīts, ka poli(3,4-etilēndioksitiofēna) izejas vadītspēja būtiski ietekmē termiski apstrādāta poli(3,4-etilēndioksitiofēna) vadītspēju. Zemas vadītspējas poli(3,4-etilēndioksitiofēna) termiskā apstrāde noved pie tā vadītspējas samazināšanās, kamēr poli(3,4-etilēndioksitiofēna) ar maksimālo vadītspēju 160 S/cm termiskā apstrāde noved pie tā vadītspējas pieauguma līdz pat vairākiem tūkstošiem S/cm. Transmisijas elektronu mikroskopija parāda, ka poli(3,4-etilēndioksitiofēna) ar šādu vadītspēju raksturo monokristālu morfoloģija.

Олга Пышкина, Алексей Кубарьков, Владимир Сергеев. Поли(3,4-этилендиокситиофен): получение и свойства.
Изучена высококонцентрационная эмульсионная полимеризация (3,4-этилендиокситиофена) в присутствии натриевой соли 2-нафталинсульфоновой кислоты в качестве допирующего агента и эмульгатора и сульфата железа(III) в качестве окислителя. Методом ИК-спектроскопии показано, что в результате такой полимеризации образуется поли(3,4-этилендиокситиофен), характеризующийся конформацией плоских бесформенных образований. Установлено, что проводимость поли(3,4-этилендиокситиофена), полученного указанным способом, сильно зависит от количества воды, пошедшей на его промывание, и проходит через максимальное значение 160 С/см. Исследовано также влияние нагревания поли(3,4-этилендиокситиофена) при 125°С на его проводимость и морфологию. Показано, что исходная проводимость поли(3,4-этилендиокситиофена) значительным образом влияет на его проводимость после нагревания. Нагревание поли(3,4-этилендиокситиофена) с низкой проводимостью приводит к ее уменьшению, в то время как нагревание поли(3,4-этилендиокситиофена) с максимальной проводимостью приводит к ее возрастанию до нескольких С/см и образованию монокристаллов, как показано методом просвечивающей электронной микроскопии.