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СИНТЕЗ ПОЛИАНИЛИНА, ПОЛИФЕНИЛЕНДИАМИНА, ПОЛИТОЛУИДИНА И ТЕКСТИЛЬНЫХ КОМПОЗИЦИОННЫХ МАТЕРИАЛОВ НА ИХ ОСНОВЕ

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Двухстадийным процессом, основанным на жидкофазной гетерогенно-каталитической гидрогенизации нитробензола, п-нитротолуола и п-нитроанилина в водном растворе 2-пропанола с получением соответствующих аминов и последующей окислительной полимеризации полученных аминов в водно-спиртовом растворе соляной кислоты в присутствии окисляющих агентов – персульфата аммония и бихромата калия были получены полианилин, политолуидин, полифенилендиамин. Структура полученных полимеров подтверждена с помощью метода ИК-спектроскопии. Исследование термических свойств полученных полимеров проводили методами термогравиметрического анализа и дифференциально-сканирующей калориметрии. Показано, что полиамины термостабильны в интервале температур 250-350 °С. Для изучения электропроводности полученных полиаминов был использован метод кондуктометрии. Показано, что при использовании бихромата калия полученный продукт обладал меньшей проводимостью по сравнению с полимером, полученным при использовании персульфата аммония. В дальнейшем, синтезированные полимеры были использованы для получения текстильных композиционных материалов на основе текстильных волокон. На первой стадии получения данных материалов хлопковое и льняное волокна были покрыты пленкой полиамида-6, как легирующей добавки, повышающей механическую прочность и фотоустойчивость. Для нанесения пленки были использованы растворы полиамида-6 в концентрированной муравьиной кислоте двух концентраций – 2,4 ммоль/л, 0,5 ммоль/л. На второй стадии на полиамидную пленку был нанесен слой обработанных полиаминов. Поверхность полученных композиционных материалов была исследована методом электронной микроскопии. Анализ волокон хлопка и льна, обработанных раствором полиамида-6 различной концентрацией показал, что при увеличении концентрации раствора полиамида возрастает упорядоченность волокон и целостность всего пучка.

Ключевые слова: полимеры, текстиль, лен, хлопок, электропроводность, красители, полианилин, полиамид-6

SYNTHESIS OF POLYANILINE, POLYPHENYLENEDIAMINE, POLYTOLUIDINE AND TEXTILE COMPOSITE MATERIALS ON THEIR BASIS

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Polyaniline, polytoluidine, polyphenylenediamine were obtained by a two-stage process based on liquid-phase heterogeneous catalytic hydrogenation of nitrobenzene, p-nitrotoluene and p-nitroaniline in an aqueous solution of 2-propanol to obtain the corresponding amines and subsequent oxidative polymerization of the resulting amines in an aqueous-alcoholic solution of hydrochloric acid in the presence of oxidizing agents - ammonium persulfate and potassium dichromate. The structure of the obtained polymers was confirmed using the method of IR spectroscopy. The thermal properties of the obtained polymers were investigated by thermogravimetry and differential scanning calorimetry. It has been shown that polyamines are thermally stable in the temperature range 250-350 °C. To investigation the electrical conductivity of the obtained polyamines, the conductometry method was used. It was shown that when using potassium dichromate, the resulting product had lower conductivity compared to the polymer obtained using ammonium persulfate. Subsequently, the synthesized polymers were used to obtain textile composite materials based on textile fibers. At the first stage of obtaining these materials, cotton and linen fibers were coated with a polyamide-6 film as an alloying additive that increases mechanical strength and photostability. To apply the membrane, we used solutions of polyamide-6 in concentrated formic acid of two concentrations - 2.4 mmol/l, 0.5 mmol/l. The surface of the obtained composite materials was examined by electron microscopy. Analysis of cotton and flax fibers treated with a solution of polyamide-6 of various concentrations showed that with an increase in the concentration of the polyamide solution, the ordering of the fibers and the integrity of the entire bundle increase.

Key words: polymers, textiles, flax, cotton, electrical conductivity, dyes, polyaniline, polyamide-6

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Nowadays textile materials are the most versatile in terms of ease of manufacture, design, traditional and new applications, as well as their flexibility, lightness and low cost [1]. Among modern forms of textiles – electronic textiles (e-textiles) are used in the form of technological gadgets in ordinary and specialized clothing to improve the quality of life and increase labor efficiency [2-5].

Smart textiles and electronic textiles are among the most promising materials for tackling the growing energy crisis. Electronic textiles are being developed using a variety of materials, including cotton [6], lyocell [7], polyester [6], nylon [8] and wool [9] - fabrics designed for use in batteries, fuel cells, supercapacitors and solar elements, as well as for the production of sensors and displays [10].

Linen textile is one of the rapidly developing branches of the textile industry in Russia and abroad. Linen and shives (casings) are used today to produce various materials for both consumer and technical purposes. The interest in the use of natural materials is understandable due to their greater environmental friendliness.

However, the use of Linen fabrics is limited to rather traditional areas of application and there is no information on the development of functional materials for a wider purpose based on Linen fiber, in contrast, for example, to cotton [11-15].

It should be noted that the majority of scientific works are devoted to the preparation and study of polyaniline [16-24], while other polyamines have received very little attention [16]. This fact determines the relevance of investigating other electrically conductive polymers based on aromatic amines.

Conductive polymers have been widely studied both for academic and industrial purposes over the past three decades, where certain interest is attributed to compositions based on polyaniline and polyamide [25-34] for the development of various devices and technologies.

Thus, the investigation of the physicochemical properties of various aromatic polyamines, as well as their use as electrically conductive coatings for linen fibers, is very important.

The task of developing a method for the production of electrically conductive polymers based on other aromatic amines is greatly facilitated by a wide base of research on the synthesis of PANI by various methods. Polyaniline is a polymer consisting of alternating oxidized (II) and reduced (I) repeating units (Fig. 1).

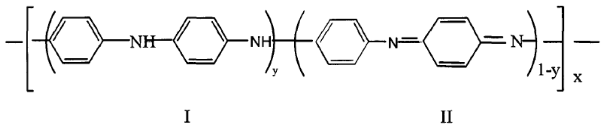


Fig. 1. Alternating oxidized (II) and reduced (I) repeating units of polyaniline

Рис. 1. Чередующиеся окисленные (II) и восстановленные (I) повторяющиеся звенья полианилина

In the process of synthesis, depending on the oxidation state, the formation of three forms of oxidized polyaniline is possible: leucoemeraldine, emeraldine, pernigraniline (Fig. 2).

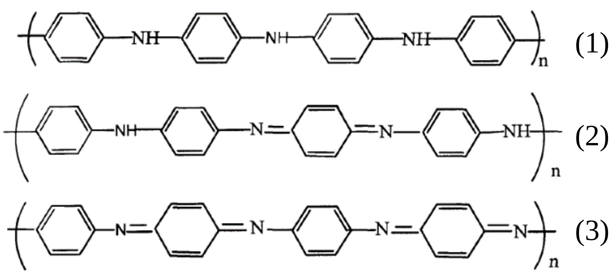
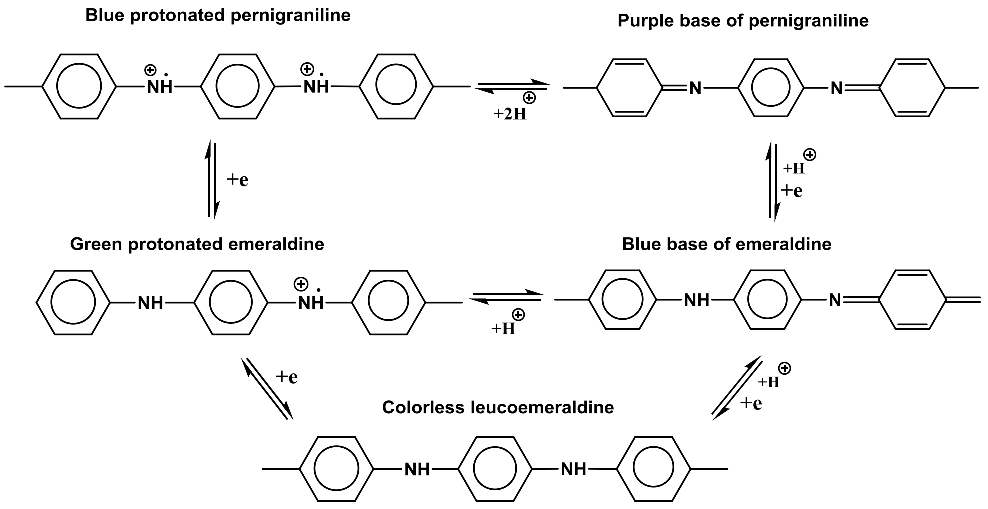


Fig. 2. The main forms of polyaniline: 1- leucoemeraldine, 2- emeraldine, 3- pernigraniline

Рис. 2. Основные формы полианилина: 1- лейкоэмеральдин, 2-эмеральдин, 3-пернигранилин

These forms of polyaniline can be in a state of equilibrium with each other through interconversions as a result of oxidation-reduction, protonation-deprotonation processes (Scheme).



Scheme. Scheme of equilibrium of polyaniline forms with each other in the processes of oxidation-reduction, protonation-deprotonation.

Схема. Схема равновесия форм полианилина между собой в процессах окисления-восстановления, протонирования-депротонирования

Each form is distinguished by its structural, physicochemical properties and also electrically conductive properties. The protonated base of emeraldine has the highest electrical conductivity.

The most studied methods for preparing emeraldine PANI are electrochemical and oxidative polymerization. A number of investigations show that, depending on the synthesis conditions, interfacial, emulsion, solid-phase polymerization are also distinguished as promising methods for producing polyaniline.

According to few studies, it is also possible to obtain PANI by a means of enzymatic polymerization in the presence of hydrogen peroxide [35-40]. During synthesis, the enzyme is responsible for oxidation and initiation of polymerization. However, a significant disadvantage of this method is that, over time the reduction of enzymes are possible (horseradish peroxidase [36-39], oxidoreductases, such as laccases [35] and peroxidases [40]) in acidic environment. As a result, there is a decrease in product yield and indicators of its electrical conductivity. Therefore, it seems more expedient to consider other variants of synthesis.

Oxidative polymerization is the most studied method of PANI synthesis based on the interaction of aniline in acidic solutions with various oxidizing agents: ammonium persulfate, potassium dichromate or ferric chloride. The most widely known and effective method is the polymerization of aniline in hydrochloric acid aqueous solution in the presence of ammonium persulfate. In this case, the product yield is 90-95% with electrical conductivity ranging from 1 to 5 Sm/cm are observed [16].

According to the IUPAC, the optimal concentration ratio of aniline and ammonium persulfate is 1:1.25. The need for a small excess of the oxidizing agent is associated with the fact that it participates not only in the initiation process, but also directly in the growth of polymer chains. As for poly-(para-phenylenediamine) and poly-(para-toluidine), the literature contains much less information on their synthesis and possible molecular structures [41, 42]. The following molecular structures are proposed as possible options – Fig. 3, 4

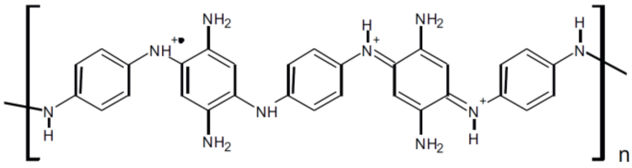


Fig. 3. The structure of poly-(para-phenylenediamine), (PpPhDA) [41]
Рис. 3. Структура полипарафенилендиамина, (ПпФДА) [41]

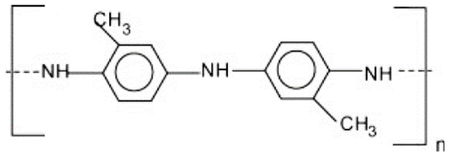


Fig. 4. The structure of poly-(para-toluidine), (PpTD) [42]
Рис. 4. Структура полипаратолуидина, (ПпТД) [42]

The poor knowledge on these objects determines the relevance of the investigation of their synthesis and properties.

Taking in account, that this method is well studied, its efficiency, simplicity of the process and its further scaling up for industrial implementation, oxidative polymerization is of greatest interest.

EXPERIMENTAL PART

Reagents and materials

For the synthesis of amines and polyamines nitrobenzene (chemically pure, JSC "VEKTON"), p-nitrotoluene (chemically pure, JSC "VEKTON"), p-nitroaniline (analytical grade, JSC "VEKTON"), 2-propanol (chemically pure, JSC "VEKTON"), catalyst 5% Pd/C (synthesized by water-alkaline hydrolysis of hydrogen tetrachloropalladate), ammonium persulfate (analytical grade, JSC" VEKTON "), potassium dichromate (analytical grade, JSC" VEKTON "), hydrochloric acid (high purity, JSC" VEKTON "), formic acid (99% of JSC" VEKTON "), polyamide-6 (industrial production, molecular weight – 21,000), Linen (LLC" Shuisky Linen ") and cotton yarn (LLC" Shuisky textiles ") were used.

Synthesis of polyamines

The synthesis of polyamines was carried out in two stages. The first stage was the liquid-phase heterogeneous catalytic hydrogenation of nitrobenzene, p-nitrotoluene, and p-nitroaniline on a 5% Pd / CAR-D catalyst in an aqueous solution of azeotropic 2-propanol to obtain the corresponding amines.

The second stage is the preparation of polyamines by the oxidative polymerization of aniline, p-toluidine, and p-phenidendiamine in 1 M aqueous-alcoholic (2-propanol) hydrochloric acid solution in the presence of ammonium persulfate or potassium dichromate as an oxidizing agent. The initial concentration of amines in a 1 M aqueous-alcoholic solution of hydrochloric acid was 0.2 mol/l. During the synthesis of PANI and PpTD, the substrate / oxidant molar ratio was 1:1.25, and for PpPhDA, 1:2.5. The resulting polymers were colored in the following colors: emerald green for polyaniline, light brown for polytoluidine, and dark brown for polyphenylenediamine.

DSC calorimetry

The study of phase transitions was carried out on a DSC 204 F 1 differential scanning calorimeter from Netzsch. The sample was placed in a pressed-in aluminum crucible with a pierced lid. The weighed portions of the sample were up to 10 mg. The measurements were carried out in a flow of argon, the gas flow rate was 15 ml/min. The samples were heated at a rate of 10 °C/min. The reference sample was an empty aluminum crucible. The measurements were carried out relative to the baseline obtained for two empty crucibles with a similar heating program. The calorimeter was calibrated by measuring the temperatures and thermal effects of phase transitions for 3 standard substances in the range from -86 to 950 °C. The error in measuring the temperature of the samples was 0.1 degrees, the sensitivity to heat flux was up to 4 μV/mW.

TG-analysis

Thermogravimetric studies were carried out on a Netzsch TG 209 F 1 microthermal balance in an argon flow, the gas flow rate was 30 ml/min. The error in determining the weight loss was $1 \cdot 10^{-3}$ mg. The samples were heated at a rate of 10 °C/min.

Processing of Linen and cotton fibers

Linen and cotton fibers were coated with polyamines to clarify the possibility of using synthesized polymers for the production of electronic textiles. The process of treatment consisted of several stages.

The first stage was to cover the fibers with a polyamide film from solutions of two different concentrations (2.4 mmol/l and 0.5 mmol/l) in concentrated formic acid to facilitate further fixation of polyamines, as well as to increase the mechanical strength and photostability of composite materials.

IR spectroscopy

The IR spectra of the polymers were obtained on an AVATAR E.S.P. spectrometer in the range of 3500-400 cm^{-1}.

Electrical conductivity

To determine the electrical conductivity of the suspensions of the obtained polyamines, an industrial portable conductometer AQUA-LAB AQ-EC100 with a high-precision electrode (AQUA-LAB, Russia) was used.

Electron Microscopy

Electronic images of fibers treated with polyamide-6 and polyamines were obtained using a digital portable electron microscope Sititech CS02 [2MPix HD 1000X] (China).

RESULTS AND DISCUSSION

Physicochemical properties of polyamines

Electrical conductivity

The value of electrical conductivity can be a property that can determine the applicability of obtained polyamines in the field of electronicts. Therefore, the electrical conductivity was measured for three obtained suspensions of polyamines using two different oxidizing agents – table.

Table

Electrical conductivity of polyamine suspensions, S/cm
Таблица. Электропроводность суспензий полиаминов, С/см

Polyamine	Oxidizing agent	
	$K_2Cr_2O_7$	$NH_4S_2O_8$
PANI	1.45 ± 0.02	2.61 ± 0.02
PpPhDA	0.12 ± 0.02	0.16 ± 0.02
PpTD	0.18 ± 0.02	0.21 ± 0.02

When using potassium dichromate, the resulting product had a lower conductivity compared to the polymer obtained using ammonium persulfate. This may be due to the fact that potassium dichromate is a stronger oxidizing agent and the oxidative polymerization process can partially proceed with the formation of a less conductive form of polyaniline, pernigraniline. In the case of polyphenylenediamine and polytoluidine preparation the electrical conductivity was also higher if ammonium persulfate was used in the synthesis of polymers.

Chemistry of polymer surface

According to the spectra, the correspondence of the materials obtained by oxidative polymerization with ammonium persulfate to aromatic polyamines was established (Fig. 5).

The broad peak in the spectra of polyamine and polyphenylenediamine at ~ 3450 cm^{-1} most likely includes several bands: ~ 3439 cm^{-1} and ~ 3420 cm^{-1} – vibrations and deformation of the N-H bond; ~ 3446 cm^{-1} stretching of the O–H bond belonging to either water molecules or 2-propanol [43]. The presence of a peak at ~ 1630 cm^{-1} indicates vibrations of the C=N bond [44].

In the case of polytoluidine, a strong shift and broadening of the peak corresponding to the vibrations and deformation of the NH bond is observed due to the presence of a larger amount of water in the polymer, as well as aliphatic stretching vibrations of the C–H bonds (~ 2921 cm^{-1} and ~ 2851 cm^{-1}) [42].

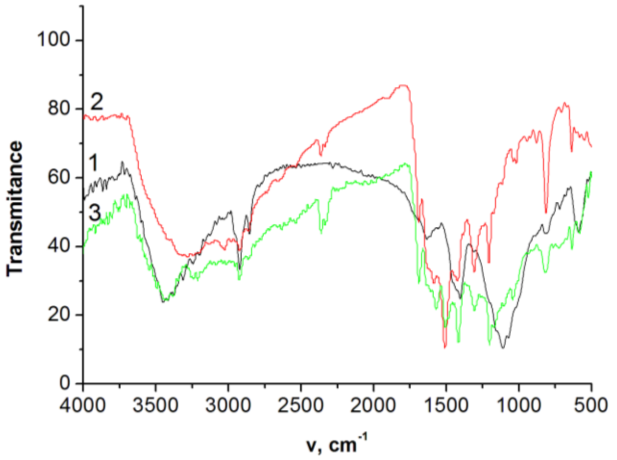


Fig. 5. IR spectra of polyamines obtained by oxidation with ammonium persulfate: 1 – PANI; 2 – PpTD; 3 – PpPhDA
Рис. 5. ИК спектры полиаминов, полученных окислением персульфатом аммония: 1 – ПАНИ; 2 – ПпТД; 3 – ПпФДА

The intense band at ~ 2920 cm^{-1} is associated with the stretching of the C-H bond in benzene, as well as the manifestation of the signal of the overtones of benzene and quinoid structural units in polyamines. The C-N valence band appears as two peaks at ~ 1384 and ~ 1254 cm^{-1}. The peak at ~ 810 cm^{-1} characterizes para-distributed aromatic rings indicating polymer formation. And the peak at ~590 cm^{-1} corresponds to para-disubstituted aromatic rings [42-44].

Combined thermal analysis (TG-DSC)

According to TGA data (Fig. 6), the thermal stability of polyamines obtained by oxidation with ammonium persulfate was: polyaniline – 250 °C; polytoluidine – 350 °C; polyphenylenediamine – 200 °C. The weight loss for each polymer was: polyaniline – 80% over the temperature range 250-350 °C; polytoluidine – 60% in the temperature range 350-700 °C; polyphenylenediamine - 40% in the temperature range 200-700°C. The delay in the mass loss of polytoluidine as compared to polyaniline may be associated with the higher stability of polytoluidine due to the formation of hydrogen bonds.

According to DSC data (Fig. 6), it can be stated that the thermal decomposition of the polymer goes through several stages: water loss (endothermic peak up to 100 °C); removal of impurities and the substituent of benzene core -NH_2 (exothermic two-stage peak in the range from 100 to 250 °C) and removal of oligomers (exothermic peak at 300 °C); degradation of polymer chains in the form of decomposition of the main polyamine chain and opening of the benzene ring (exothermic peak from 400 to 700 °C) [45, 46].

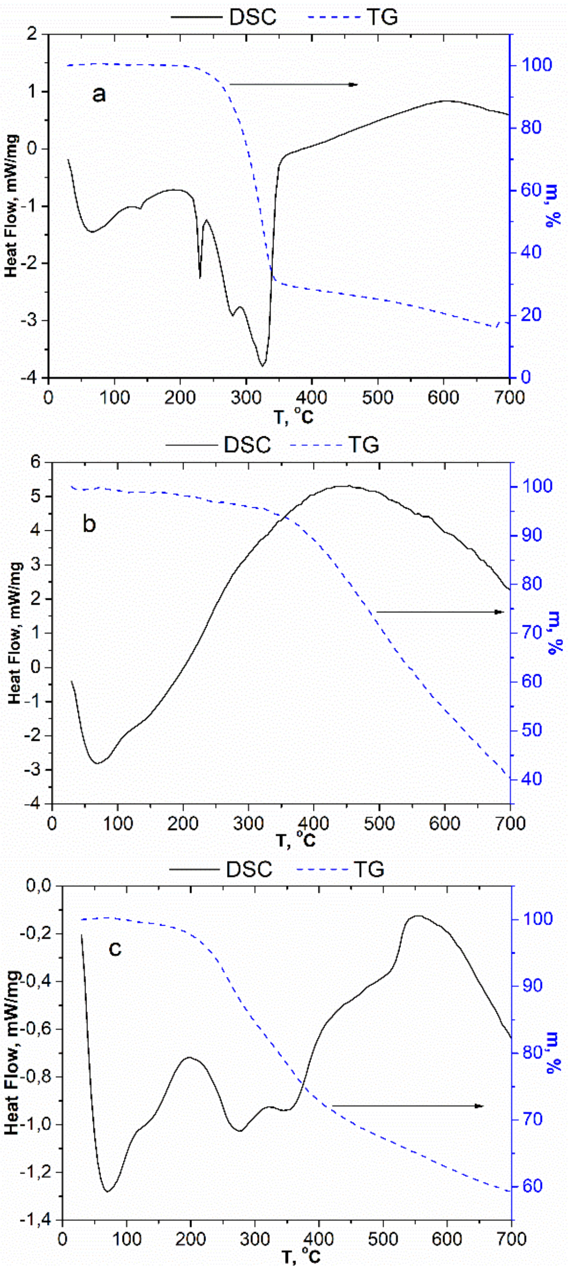


Fig. 6. Data of combined thermal analysis of polyamines obtained by oxidation with ammonium persulfate: a – PANI; b – PpTD; c – PpPhDA;

Рис. 6. Данные совмещенного термического анализа полиаминов, полученных окислением персульфатом аммония: a – ПАНИ; b – ПпТД; c – ПпФДА

Structure and processing quality of fibers

Using electron microscopy, images of Linen and cotton fibers, pre-coated with a polyamide film and treated with polyamines produced by oxidation with ammonium persulfate and untreated fibers of Linen and cotton were obtained (see supplementary material).

Untreated fibers are less ordered due to the presence of breaks and fiber fragments. A comparative analysis of cotton fibers treated with a solution of polyamide-6 (PA) of various concentrations showed that when using a more concentrated PA solution, the fiber ordering and the integrity of the entire bundle increase. A similar picture is observed in the case of Linen fibers.

The obtained images showed a more uniform coating of Linen and cotton fibers with polytoluidine and polyphenylenediamine. Whereas polyaniline is partially present on the surface of the fibers in the form of particles and their agglomerates. Due to the latter, the green color of the fibers is less regular.

CONCLUSIONS

The preparation of polyaniline (PANI), poly-(para-toluidine) (PpTD), poly-(para-phenylenediamine) (PpPhDA) and textile composite was successfully performed by oxidative polymerization method and wetting of linen and cotton fibers by polyamide-6 and polyamines was confirmed by IR-spectroscopy.

According to the electrical conductivity data, ammonium persulfate is the best oxidizing agent for polyaniline production, while for polytoluidine and polyphenylenediamine, the difference in results in the case of using ammonium persulfate or potassium dichromate is not so great. The highest electrical conductivity was found for polyaniline.

Thermal analysis shows acceptable thermal stability of polyaniline (PANI), poly-(para-toluidine) (PpTD), poly-(para-phenylenediamine) (PpPhDA).

According to electron microscopy data, a more uniform coating of Linen and cotton fibers was observed for poly-(para-toluidine) (PpTD), poly-(para-phenylenediamine) (PpPhDA).

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