PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2023, **57**(3), p. 190–198

Chemistry

CONDUCTIVE POLYMERS AS MATERIALS USED IN SENSORS FOR DETERMINATION OF IMPORTANT VOLATILE COMPOUNDS IN THE FIELD OF FOOD SAFETY

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In the field of food safety, sensors are widely used for the detection and determination of a wide variety of volatile compounds. This work presents the synthesis of a number of polyaniline analog polymers and the study of their properties as such sensors. In the course of the work, the design and preparation of carriers for polymers with sensor properties was carried out and, based on it, a new method for measuring and recording changes in the electrical conductivity of insoluble polymers in the presence of volatile substances was developed. The applicability of the developed method was verified.

https://doi.org/10.46991/PYSU:B/2023.57.3.190

Keywords**:** food safety, sensors, benzidine, o-anisidine, polyaniline.

Introduction. One of the currently available methods for determining food freshness is based on expiration dates, which are often considered unreliable, and another on time-temperature quality indicators (TTI), which can be expensive and do not provide true data on bacterial activity. Various types of sensors have also been widely used in recent years to evaluate food freshness. One of those is a sensor based on a conductive polymer film, which reacts with volatile substances released from selected foods. As a result of food biodegradation, gases and vapors are released, which is confirmed by the use of gas chromatography and SWIFT-MS analytical methods. Under the influence of various food volatile mixtures, the sensor exhibits quantitative changes in color, conductivity, etc., which are specific and easily measurable [1].

A well-known example of conducting polymers are polyacetylene, polypyrole, polythiophene and polyaniline, which are also known as conjugated polymers from the literature [2, 3]. Polyaniline has excellent thermal stability and provides good electrical conductivity [4]. Aniline is much more economically available than any other monomer used for the synthesis of conjugated polymers, which leads to the widespread use of this polymer [5–7]. The synthesis of polyaniline is also much simpler compared to other conjugated polymers. Polyaniline is produced either

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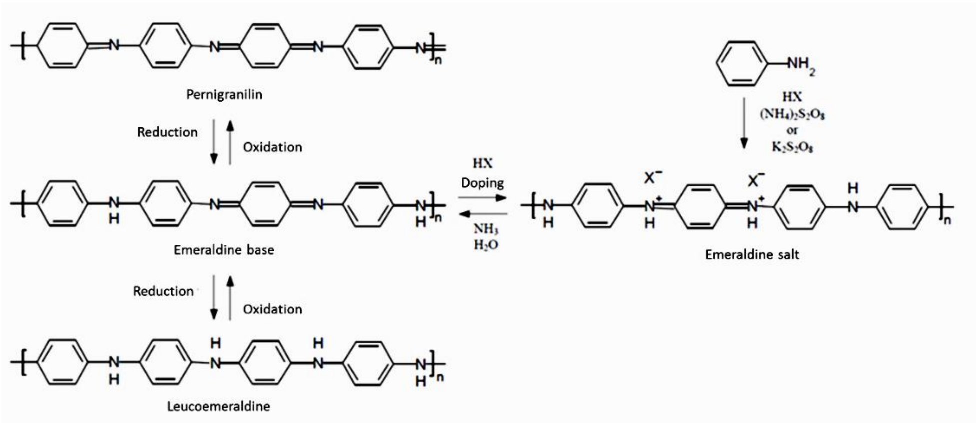
chemically or electrochemically. Recently, there has been increased research interest in the use of this polymer as a sensor. This is due to the ability of the polymer to interact with different types of gas or vapor, which in turn affects the conductivity or color of polyaniline. The structure, preparation and doping process of polyaniline are schematically depicted in Scheme.



Scheme. Chemical structure, synthesis, acid/base doping/de-doping and redox conversion of polyaniline [1].

Many studies have been conducted on the application of polyaniline as a sensor for various gases such as hydrogen, ammonia, carbon dioxide, and carbon monoxide [8–11]. It has been found that polyaniline can change its color and resistance under the influence of various reagents, as well as undergo various other changes. Many studies have also been done on the use of polyaniline as a sensor for volatile compounds [12–14]. The aim of the work is to expand the field of application of polyaniline analog polymers to verify their use as sensors in food quality control processes.

Materials and Methods. In the previous works, the study of the conductivity of semiconducting polymers synthesized by us was performed according to Fig. 1 [15].

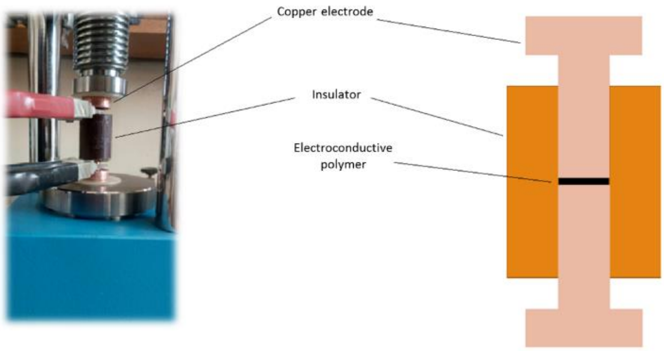


Fig. 1. The old method for electrical conductivity measurements.

In this work, the goal was the determination of the change in electrical conductivity in the presence of volatile substances in the environment, therefore it was impossible to apply the above scheme, because in that case the polymer had no contact surface with the volatile substance. For the presented work, a new method was developed for insoluble polymers, the scheme and image of the obtained samples are presented in Fig. 2.

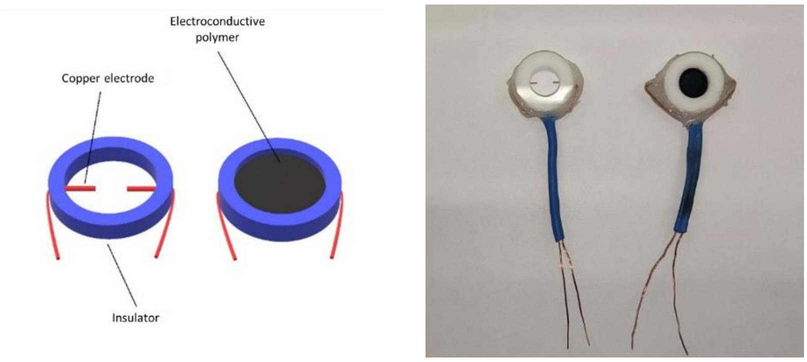


Fig. 2. The modeled structure and obtained samples.

The sensors were prepared by pressing polymer powder onto a carrier part, as the obtained polymers were insoluble. The sensor structure was designed with an open surface (to provide a contact surface with the volatile substances to be determined) and a polymer-conductor contact to measure resistance changes. The mentioned construction allowed to make the measurements of the dependence of the resistance change on the concentration of volatile substances.

***Synthesis of Polyaniline Analog Polymers*.** The synthesis was carried out by oxidation-condensation of benzidine, benzidine sulfate and o-anisidine monomers of different molar ratios (P1, P2, P0.5) with the same molar ratio of ammonium persulfate using glacial acetic acid-methanol mixture as a solvent. Polyaniline was also synthesized under the conditions taken from the literature as a comparative sample. The synthesized polymers were doped with hydrochloric acid aqueous solutions and dried in a vacuum.

***Spectral Analysis*.** The spectral analysis has been performed using a PG Instruments T60 UV-Vis spectrometer. As the polymers were insoluble, the corresponding oligomers, which were the side products of the synthesis, were used.

***Thermogravimetric Studies*.** The thermal stability of the obtained polymers was measured using a STA 449 F3 Jupiter/QMS 403 QUADRO Aeolos thermo-gravimeter coupled with a mass spectrometer.

***Fabrication of Sensors from Synthesized Polymers and Evaluation of Sensor Properties*.** A series of measurements of the change in electrical conductivity and concentration dependence of volatiles were performed. Acetone and methanol were selected as volatile substances. The experiments were performed in a test tube of known volume at a constant temperature (Fig. 3).

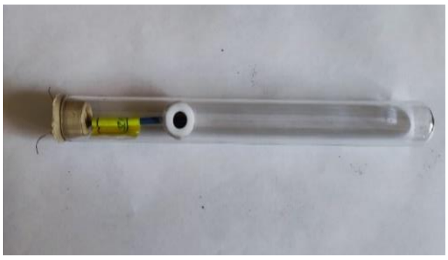


Fig. 3. Sensor in an airtight test tube.

The concentration of volatile substances (*ppm*) was determined by the following equation:

$$C_{(\text{vol.comp.})} = \frac{\rho_{(\text{vol.comp.})} V_{(\text{vol.comp.})} RT}{M_{(\text{vol.comp.})} P V_{(\text{test tube})}},$$

where the volume of the test tube ($V_{(test\ tube)}$) was determined with the help of a burette (accuracy of 0.1 *mL*), measuring the volume of water placed in the test tube. The test tube was brought to a constant temperature (at which the volatiles completely transited to the gas phase) and held until the sensor equilibrated, then a certain amount of the volatile was added and the resistance changes were recorded.

Resistance measurements were made using an Applent AT512 Precision Resistance Meter equipment, which uses the "4-wire resistance measurement" method. The electroconductivity of polymers was calculated by Pouillet's law [16]. The scheme of the experiment setup is shown in Fig. 4.

Acetone and methanol, which are toxic and quantitatively highly controlled in various food production processes, were chosen for the experiments [17, 18].

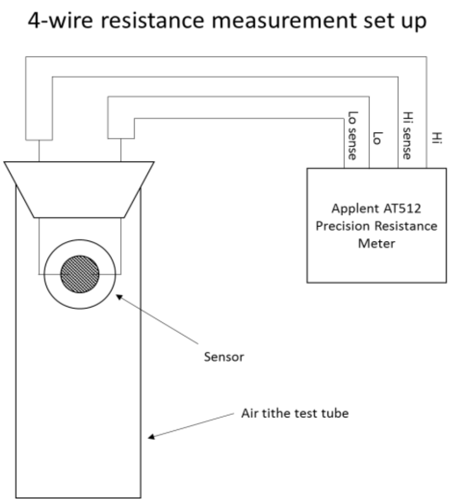


Fig. 4. System for conductivity measurement.

Results and Discussion. Based on the fact that polyaniline has a wide application in sensors, it was aimed to check the sensor properties of new polyaniline analog polymers. The fact that the polymers have an analogous structure was confirmed by the UV-Vis spectral method. It is known that the trimer obtained by oxidation of benzidine by polycondensation method has absorption at 375 *nm* and 472 *nm* wavelengths, and the absorption characteristics of polyanisidine are expressed at 318 *nm* and 608 *nm* wavelengths [15].

The results of the spectral analysis are shown in Fig. 5.

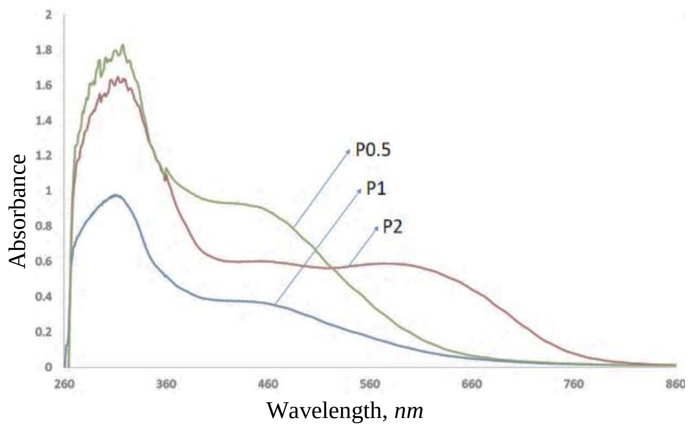


Fig. 5. Results of spectral studies of the corresponding oligomers P1, P2, P0.5.

By comparing the absorption bands of oligomers of obtained samples with the UV-Vis spectra of polyaniline from the literature, we confirmed that the synthesized polymers have partially different structure from polyaniline [19].

The thermograms, as well as the data obtained from a mass spectrometer for fragments or evolved gases, are shown in Fig. 6, a–c.

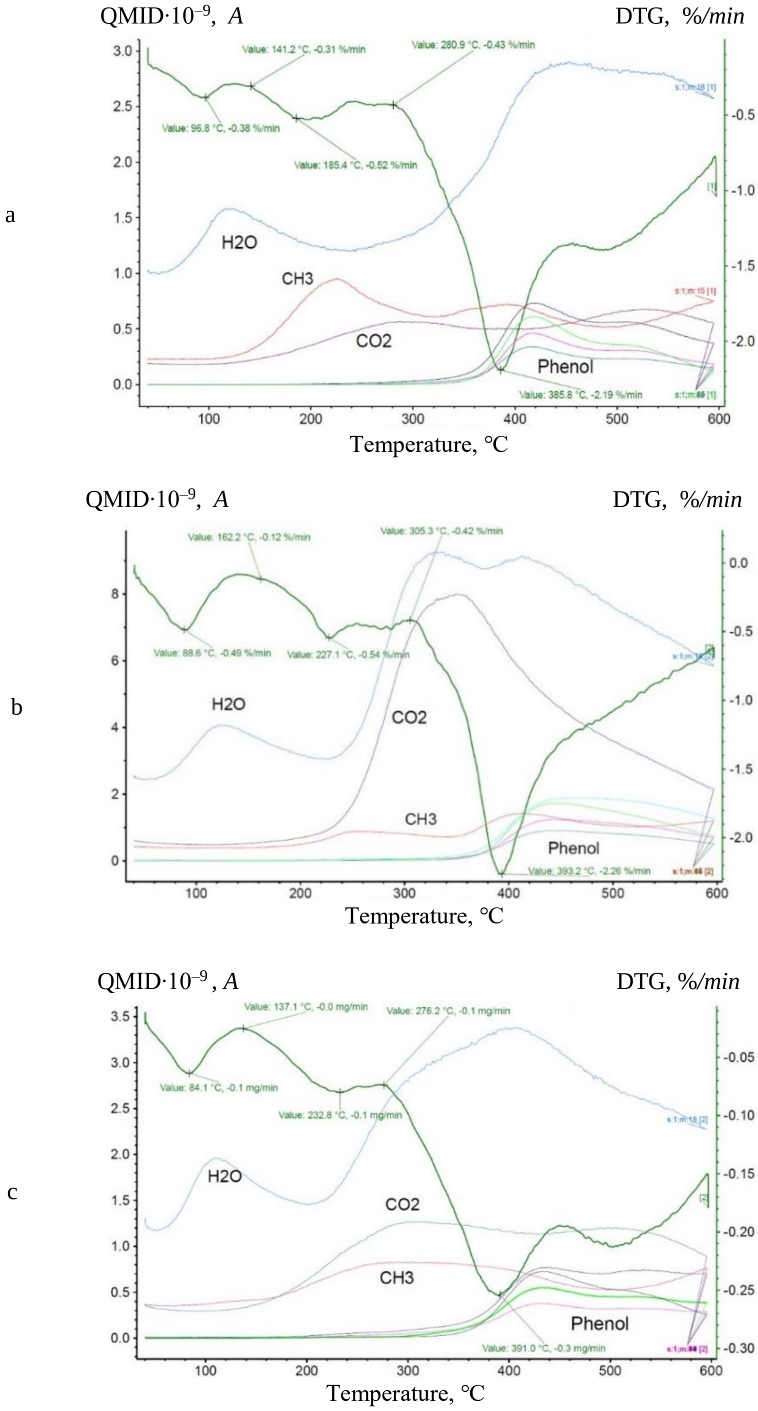


Fig. 6. Thermograms of P1 (a), P2 (b), P0.5 (c) and mass spectrometer data.

The thermal stability and electrical conductivity of the obtained polymers are shown in Table.

Degradation starting points and electrical conductivity of polymers

Polymer	Degradation starting point, °C	Conductivity, *σ*, *S·m*$^{-1}$
P1	281	$1.524 \cdot 10^{-4}$
P2	305	$2.567 \cdot 10^{-4}$
P0.5	276	$1.148 \cdot 10^{-5}$

As can be seen from the data obtained, depending on the change in the ratio of monomers, the thermal stability and electrical conductivity of copolymers also change.

The dependence of conductivity on the concentration of volatile compounds is presented in Fig. 7.

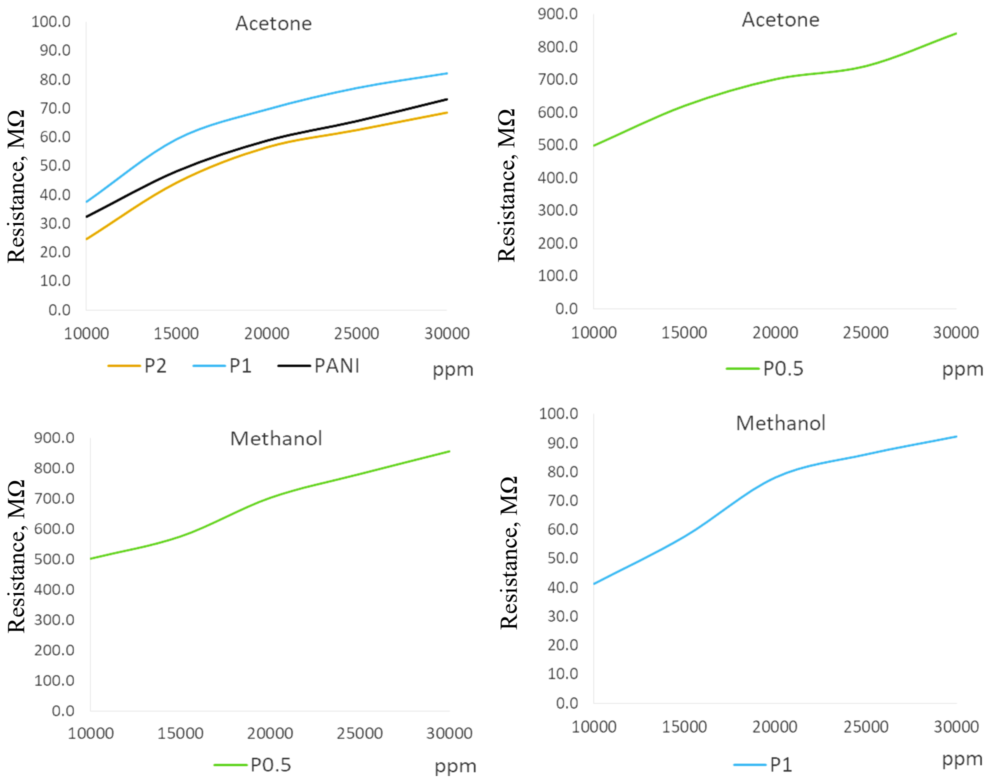


Fig. 7. Dependence of conductivity on the concentration of a volatile substance.

Polyaniline, which is a reference sample for the obtained polymers, was synthesized by a well-known method taken from the literature [20]. According to literature data, it should also show sensor sensitivity to methanol, but as a result of experiments, the absence of these properties was observed [14].

The graphs show the dependency of conductivity on the concentration, as the concentration increases the conductivity decreases. Form the data obtained, it can be noticed that only P1 and P0.5 polymers showed sensitivity towards methanol. All polymers were sensitive to acetone. Based on the thermogravimetric data and electrical conductivity values of polymers, the tendency of decrease in thermal stability and electrical conductivity can be interpreted by the reduction of quinonediimine units in the polymer structure.

Conclusion. A new method of electrical conductivity measurement has been developed for the insoluble polymers, which at the same time allowed to evaluate the sensory properties of the obtained polymers. The connection between the polymer structure and its thermal stability and electrical conductivity has been shown. The dependence of the conductivity of the polymers on the concentration of volatile compounds has been shown. The dependency is inversely proportional. The sensitivity of the polymers towards the volatile compounds has been noticed to differ from each other, as a consequence of the higher content of quinonediimine units. This indicates that the selectivity can be achieved by controlling the polymer structure. Thus, this research has shown that the polyaniline analog polymers have sensitivity and can be used as sensors.

Received 26.06.2023
Reviewed 04.09.2023
Accepted 18.09.2023

REFERENCES

1. Li D., Huang J., Kaner R.B. Polyaniline Nanofibers: A Unique Polymer Nanostructure for Versatile Applications. *Acc. Chem. Res.* **42** (2009), 135–145. https://doi.org/10.1021/ar800080n
2. Bolto B.A., McNeill R., Weiss D.E. Electronic Conduction in Polymers. III. Electronic Properties of Polypyrrole. *Aust. J. Chem.* **16** (1963), 1090–1103. https://doi.org/10.1071/CH9631090
3. Pron A., Rannou P. Processible Conjugated Polymers: from Organic Semiconductors to Organic Metals and Superconductors. *Prog. Polym. Sci.* **27** (2002), 135–190. https://doi.org/10.1016/S0079-6700(01)00043-0
4. Chiang J.-Ch., MacDiarmid A.G. Polyaniline: Protonic Acid Doping of the Emeraldine form to the Metallic Regime. *Synth. Met.* **13** (1986), 193–205. https://doi.org/10.1016/0379-6779(86)90070-6
5. Feast W.J., Tsibouklis J., et al. Synthesis, Processing and Material Properties of Conjugated Polymers. *Polymer* **37** (1996), 5017–5047. https://doi.org/10.1016/0032-3861(96)00439-9
6. Bhadra, S., Khastgir, D., et al. Progress in Preparation, Processing and Applications of Polyaniline. *Prog. Polym. Sci.* **34** (2009), 783–810. https://doi.org/10.1016/j.progpolymsci.2009.04.003
7. Gospodinova N., Terlemezyan L. Conducting Polymers Prepared by Oxidative Polymerization: Polyaniline. *Prog. Polym. Sci.* **23** (1998), 1443–1484. https://doi.org/10.1016/S0079-6700(98)00008-2
8. Grzeszczuk M. Electrochemical Study of Polyaniline Film Electrodes and their Modifications – Impedance Spectroscopy Measurements on Hydrogen Evolution Reaction. *Electrochim. Acta* **39** (1994), 1809–1816. https://doi.org/10.1016/0013-4686(94)85169-7
9. Hong K.H., Oh K.W., Kang T.J. Polyaniline-Nylon 6 Composite Fabric for Ammonia Gas Sensor. *J. Appl. Polym. Sci.* **92** (2004), 37–42. https://doi.org/10.1002/app.13633

10. Irimia-Vladu M., Fergus J.W. Suitability of Emeraldine Base Polyaniline-PVA Composite Film for Carbon Dioxide Sensing. *Synth. Met.* **156** (2006), 1401–1407. https://doi.org/10.1016/j.synthmet.2006.11.005
11. Dixit V., Misra S.C.K., Sharma B.S. Carbon Monoxide Sensitivity of Vacuum Deposited Polyaniline Semiconducting Thin Films. *Sens. Actuators B Chem.* **104** (2005), 90–93. https://doi.org/10.1016/j.snb.2004.05.001
12. Kim J., Sohn S., Huh J. Fabrication and Sensing Behavior of PVF2 Coated-Polyaniline Sensor for Volatile Organic Compounds. *Sens. Actuators B Chem.* **108** (2005), 409–413. https://doi.org/10.1016/j.snb.2004.11.072
13. Lee K.M., Yu J.B., et al. Volatile Organic Gas Recognition Using Conducting Polymer Sensor Array. *Eco-Materials Processing & Design (ISEPD)* **439** (2003), 344–351. https://doi.org/10.4028/www.scientific.net/MSF.439.344
14. Hwang H.R., Roh J.G., et al. Sensing Behaviour of the Polypyrrole and Polyaniline Sensor for Several Volatile Organic Compounds. *Met. Mater. Int.* **9** (2003), 287–291. https://doi.org/10.1007/BF03027048
15. Durgaryan A.H., Durgaryan N.A., et al. Syntheses and Investigation of Polymers Containing 1-Triazene-1,3-diyl and 1,4-Phenylene Group. *Synth. Met*. **160** (2010), 180–186. https://doi.org/10.1016/j.synthmet.2009.10.029
16. Montoya N.A., Criscuolo V., et al. Twin-Wire Networks for Zero Interconnect, High-Density 4-Wire Electrical Characterizations of Materials. *Research* **2022** (2022). University of Rome Tor Vergata. Article number 9874249. https://doi.org/10.34133/2022/9874249
17. Fishbein Dr.L. *Environmental Health Criteria 196: Methanol.* World Health Organization, Geneva. ISBN 92 4 157196 9 (NLM Classification: QV 83) (1997).
18. Nhu-Thuc Phan, Ki-Hyun Kim, et al. Analysis of Volatile Organic Compounds Released during Food Decaying Processes. *Environ. Monit. Assess.* **184** (2012), 1683–1692. https://doi.org/10.1007/s10661-011-2070-2
19. Vadiraj K.T., Belagali S.L. Characterization of Polyaniline for Optical and Electrical Properties. *IOSR J. Appl. Chem.* **6** (2018), 1555–1560. https://doi.org/10.22214/ijraset.2018.6227
20. Noby H., El-Shazly A.H., et al. Strong Acid Doping for the Preparation of Conductive Polyaniline Nanoflowers, Nanotubes, and Nanofibers. *Polymer* **182** (2019), Article number 121848. https://doi.org/10.1016/j.polymer.2019.121848

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ՀԱՂՈՐԴԻՉ ՊՈԼԻՄԵՐՆԵՐԸ, ՈՐՊԵՍ ՆՅՈՒԹԵՐ, ՈՐՈՆՔ ԿԻՐԱՌՎՈՒՄ ԵՆ ՍԵՆՍՈՐՆԵՐՈՒՄ ՍՆՆԴԻ ԱՆՎՏԱՆԳՈՒԹՅԱՆ ՈԼՈՐՏՈՒՄ ՑՆԴՈՂ ՄԻԱՑՈՒԹՅՈՒՆՆԵՐԻ ՈՐՈՇՄԱՆ ՀԱՄԱՐ

Սննդի անվտանգության ոլորտում սենսորները լայնորեն կիրառվում են տարբեր տեսակի ցնդող միացությունների հայտնաբերման և նույնականացման համար: Այս աշխատանքում ներկայացված է պոլիանիլինի անալոգ կառուցվածքի մի շարք պոլիմերների սինթեզը և դրանց հատկությունների ուսումնասիրությունը՝ որպես տվիչներ: Աշխատանքի ընթացքում իրականացվել են սենսորային հատկություններով պոլիմերների կրիչների նախագծում և պատրաստում, և դրա հիման վրա մշակվել է ցնդող նյութերի առկայությամբ չլուծվող պոլիմերների էլեկտրահաղորդունակության փոփոխության չափման և գրանցման նոր մեթոդ: Փորձարկվել է մշակված մեթոդի արդյունավետությունը:

М. С. ТОРОСЯН, Н. А. ДУРГАРЯН

ПРОВОДЯЩИЕ ПОЛИМЕРЫ КАК МАТЕРИАЛЫ, ИСПОЛЬЗУЕМЫЕ В СЕНСОРАХ ДЛЯ ОПРЕДЕЛЕНИЯ ВАЖНЫХ ЛЕТУЧИХ СОЕДИНЕНИЙ В ОБЛАСТИ ПРОДОВОЛЬСТВЕННОЙ БЕЗОПАСНОСТИ

В области безопасности пищевых продуктов широко используются сенсоры для обнаружения и определения самых разнообразных летучих соединений. В данной работе представлены синтез ряда полимеров-аналогов полианилина и исследование их свойств в качестве таких сенсоров. В ходе работы выполнено проектирование и приготовление носителей для полимеров с сенсорными свойствами, и на их основе разработан новый метод измерения и регистрации изменения электропроводности нерастворимых полимеров в присутствии летучих веществ. Проверена работоспособность разработанного метода.