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One-Step Synthesis of Functional Sulfonated Polynaphthoylenebenzimidazoles for Biosensing Applications

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Abstract: Polynaphthoylenebenzimidazoles containing functional sulfo groups were synthesized by a one-step method in a sulfuric acid medium with oleum. A polymer-analogous transformation of these polymers with aqueous solutions of metal salts (K, Ca, and Cr) was carried out. Their chemical structure was characterized by FTIR, NMR, and elemental analysis. Polymer salt coatings were deposited on QCM sensor surfaces by electron beam-induced vacuum deposition. The morphology of the coatings was characterized by AFM. It was shown that the coatings formed from a series of polymer salts have different adsorption activity in acetaminophen–water solution compared to distilled water. The QCM results indicate that sensor signal correlates with polymer coating thickness, morphology, and its chemical composition.

Keywords: polyheteroarylenes; sulfonated polynaphthoylenebenzimidazoles; electron beam dispersion in vacuum; sensors

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Citation: Bulycheva, E.G.; Belomoina, N.M.; Begunov, R.S.; Nikiforova, G.G.; Vasil'ev, V.G.; Gainutdinov, R.V.; Yablokov, M.Y.; Buzin, A.I.; Buzin, M.I. One-Step Synthesis of Functional Sulfonated Polynaphthoylenebenzimidazoles for Biosensing Applications. *Appl. Sci.* **2023**, *13*, 1073. https://doi.org/10.3390/app13021073

Academic Editor: Fabio Di Pietrantonio

Received: 21 December 2022
Revised: 11 January 2023
Accepted: 11 January 2023
Published: 13 January 2023

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1. Introduction

Previously developed methods for the synthesis of various heat-resistant polyheteroarylenes (PHA) arose due to the needs of modern technology. As a rule, these are polymers with rigid chains containing stable heterocycles such as polyimides, polybenzimidazoles, and polyoxadiazoles and exhibiting high thermal stability, fire and chemical resistance, and hydrolytic and radiation resistance [1–3]. Their synthesis is carried out in solid phase, in phenolic or amide solvents at high temperatures during a long period of time [1–3]. It should be noted that polynaphthoylenebenzimidazoles (PNBIs) are distinguished among PHAs by their unique properties, although this type of PHA is the least studied [4,5] due to the complexity of its synthesis and processing.

Modification of the chemical structure of PNBI by the introduction of sulfo groups is of considerable interest in terms of the creation of new materials with valuable properties [6]. The well-known two-stage method for the preparation of sulfonated PNBI (SPNBI) is very laborious. They are obtained by a polymer-analogous reaction of PNBI sulfonation with oleum–sulfuric acid mixture [6]. Therefore, the development of a more technologically advanced synthesis of SPNBI is of undoubted scientific and applied interest.

SPNBI can be considered as potentially effective precursors of heat-resistant polymeric ionomers. Another promising application of SPNBIs is their use as a sensitive layer for multisensor systems. The main idea of this approach is to use an array of sensors with weak selectivity and slightly different responses to various analytes. The array of sensors and

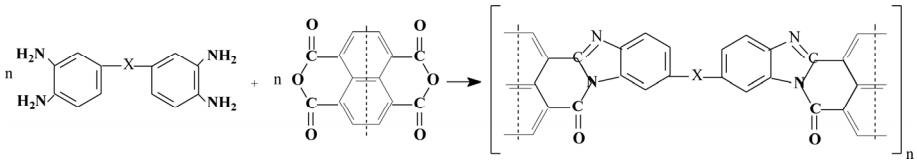
computer processing of the "fingerprint" type response make it possible to detect various substances in a gas and water environment. The development of a multisensor system including a set of sensors, or biosensors, for the recognition of hazardous substances, food products, and drugs is a promising scientific and technical task [7–9].

In this work, we propose to use SPNBI and ionomers based on them as coatings for quartz crystal microbalance (QCM) sensors. There are a lot of various applications of QCM sensors in the literature [10–12], but they are mainly related to the recognition of substances in the gas phase and there are only few examples of their use for the analysis of liquids [13,14]. One of the reasons is the low adhesion of coatings to the surface of sensors and the solubility of polymer coatings of QCM sensors in liquid media.

Thus, the aim of this work was to develop an alternative method for the one-stage synthesis of PNBI with attached functional sulfo groups and to create ionomers based on them by replacing hydrogen in sulfo groups with metal ions, as well as to study their applicability as a sensitive layer for multisensor systems.

2. Results and Discussion

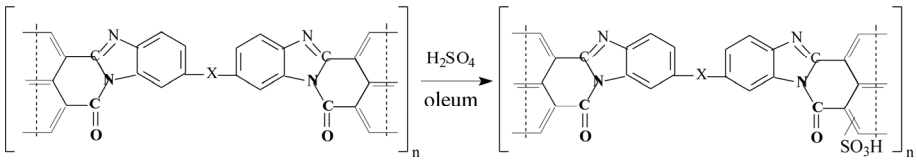
A well-known method for preparing PNBI involves a high-temperature catalytic polyheterocondensation reaction in high-boiling phenolic solvents [15,16] (Scheme 1).



Scheme 1. General synthesis scheme of polynaphthoylenebenzimidazoles.

However, the lack of a developed monomer base holds back the progress in the synthesis and use of these representatives of PHA. In this work, we used 3,3′,4,4′-tetraaminodiphenyl oxide [17] and 1,3-bis(3,4-diaminophenoxy)benzene [18] as tetraamines and dianhydride 1,4,5,8-naphthalenetetracarboxylic acid and 1,3-bis(1,8-dicarboxynaphthoyl-4)benzene dianhydride [19] as anhydride components.

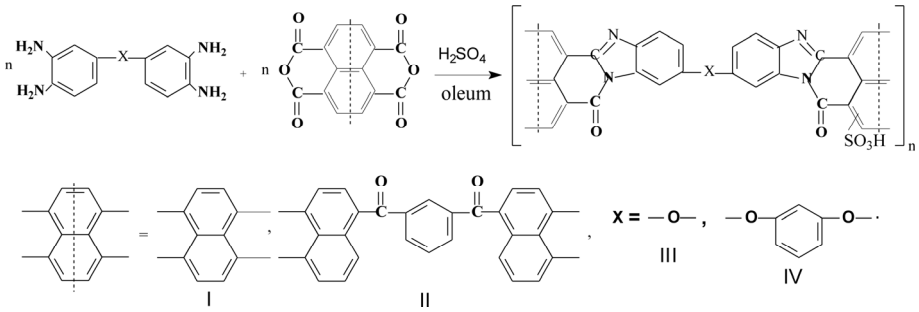
In earlier work [6], a polymer-analogous sulfonation reaction of preliminarily synthesized PNBIs with an oleum–sulfuric acid mixture was used for functional PNBIs isolation as shown in Scheme 2.



Scheme 2. Traditional method of synthesis of sulfonated polynaphthoylenebenzimidazoles.

Since the reaction of formation of the naphthoylenebenzimidazole ring proceeds in an acidic medium, it seemed appropriate to investigate a one-step method for the synthesis of functional SPNBI directly from the starting monomers in a sulfuric acid–oleum mixture, which plays the role of solvent, and sulfurizing as well as dehydrating agent (Scheme 3). This method allows to avoid environmentally hazardous chemicals such as phenol, cresol, p-chlorophenol, and amide solvents; lower the reaction temperature from 180 °C to 120 °C; eliminate the stages of precipitation and extraction of PNBI with large volumes of methanol; and finally to reduce energy costs.

For the first time, we have developed a one-stage method for the synthesis of SPNBI in accordance with the following reaction scheme.



Scheme 3. Alternative one-step method of synthesis of sulfonated polynaphthoylenebenzimidazoles.

It is known that the parameters of the polycyclocondensation reaction significantly affect the process of polymer formation. Therefore, the effect of temperature, reaction time, and the ratio of the sulfurizing agents on the properties of the final polymer was studied.

Under the most favorable conditions, a number of SPNBIs were synthesized. In the course of the reaction, we measured their characteristics such as sulfur content according to elemental analysis (*S*) and reduced viscosity (η_{red}), which are summarized in Table 1.

Table 1. One-step synthesis conditions and properties of sulfonated polynaphthoylenebenzimidazoles.

Polymer *	Reaction Time, Hours					
	3		5		11	
	S **, wt.%	η_{red} ***, dL/g	*S* **, wt.%	η_{red} ***, dL/g	*S* **, wt.%	η_{red} ***, dL/g
SPNBI-I,III ****	0.6	-	2.1	-	5.9	0.4
SPNBI-II,III	1.1	0.1	2.5	0.2	4.8	0.2
SPNBI-II,IV	1.7	0.1	2.7	0.2	6.3	0.3

* The starting materials for synthesis correspond to those given in Scheme 3. ** Sulfur content according to elemental analysis, wt.%. *** Reduced viscosity η_{red}, measured in N-methylpyrrolidone (N-MP) at 25 °C, at a concentration of 0.5 g/dL. **** Partially soluble in N-MP.

The study of SPNBIs synthesized showed that their IR spectra exhibit absorption maxima at 1615 and 1547 cm^{-1}, which are characteristic for C = N absorption band and at 1700 cm^{-1} assigned to C = O group of the benzimidazole cycle [20]. Additionally, a band at 1055 cm^{-1} observed in the IR spectra is characteristic for the stretching vibrations of SO_3 groups in sulfonic acids.

The synthesized SPNBIs were examined by solid-state ^{13}C NMR spectroscopy (Figure 1). The NMR spectra contain broad peaks in the range of 140–120 ppm, which correspond to the signals of carbon atoms of the benzimidazole ring, according to the data of [21].

For a more accurate determination of the structure of the synthesized polymers, a ^{13}C NMR spectrum of SPNBI-I,III in D_2SO_4 was obtained (Figure 2).

In the ^{13}C NMR spectrum of SPNBI-I,III signals of C = O and C = N groups (157.90 and 148.00, 147.6 ppm, respectively) are observed as well as signals assigned to carbon atoms of the benzimidazole ring at 136.59 and 127.88 ppm. The data obtained are in good agreement with the results of the work [21].

The structure of the monomers used affects the properties of the resulting functional polymers. SPNBIs based on dianhydride I are soluble in N-MP only when the sulfur content is more than 4.8 wt.%. SPNBIs based on dianhydride II begin to dissolve in N-MP at a low (1.1 wt.%) sulfur content in their composition.

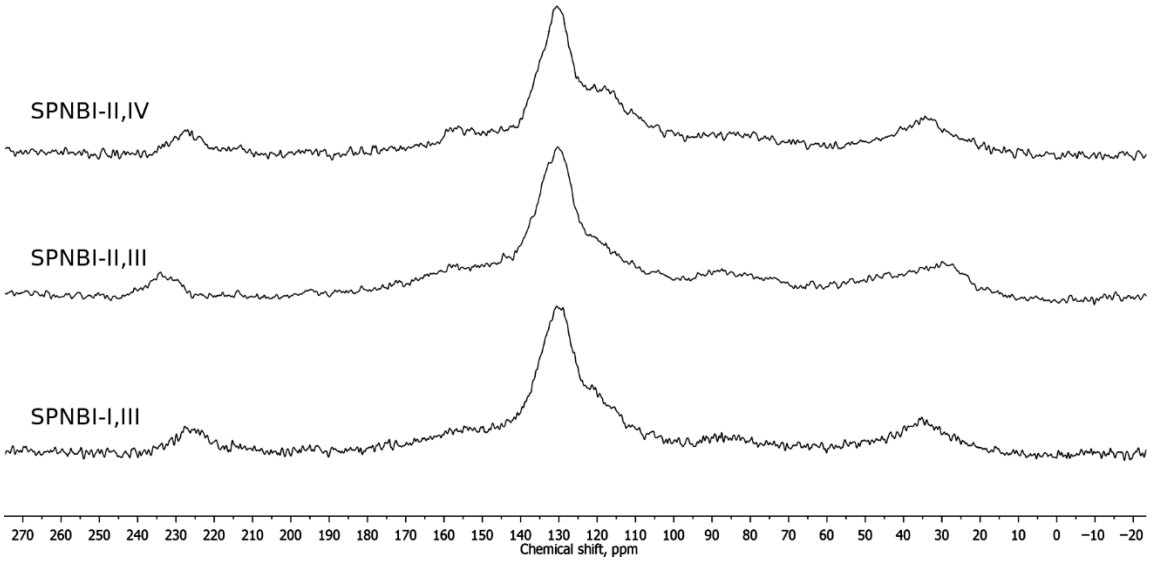


Figure 1. Solid-state ^{13}C NMR spectra for synthesized polymers.

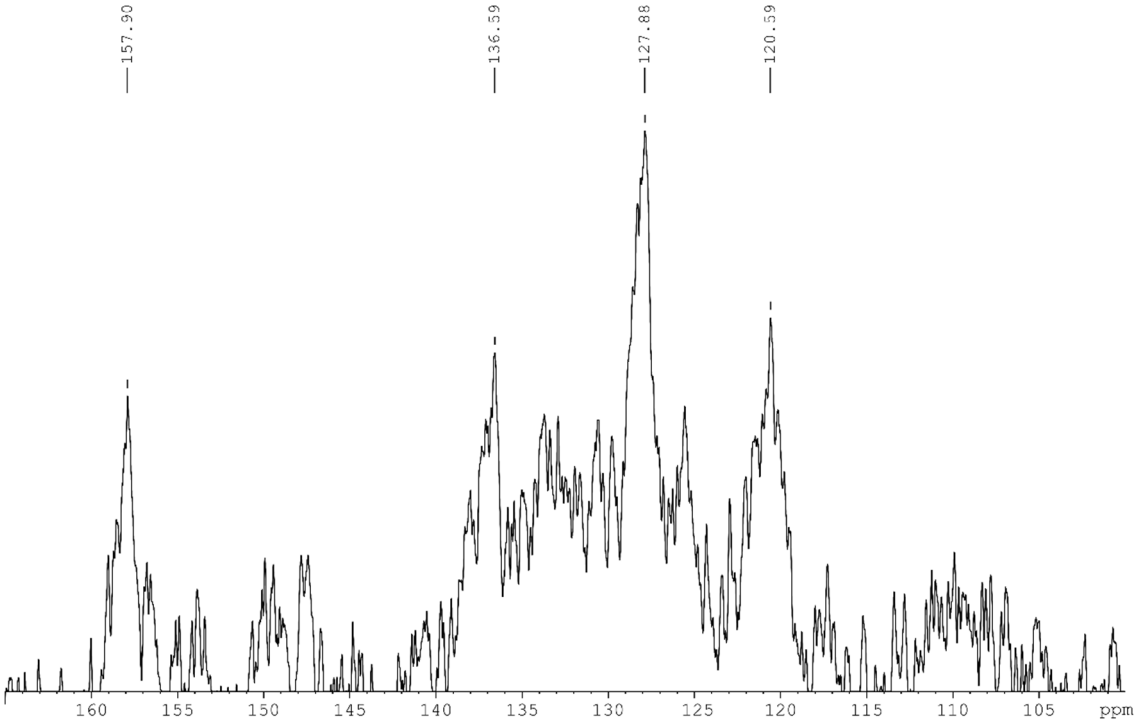


Figure 2. ^{13}C NMR spectrum for SPNBI-I,III in D_2SO_4.

The data of elemental analysis, the reduced viscosity, and IR spectroscopy indicate that under the conditions used (sulfuric acid:oleum 3:1, 120 °C), the cyclopolycondensation between bis-naphthalic anhydrides and tetraamines and sulfonation of the resulting polymers occur simultaneously, leading to the formation of functional SPNBIs.

SPNBI-I,III was chosen for electrophysical studies in terms of biosensing applications and obtaining of solid ionomers, because of its limited solubility in N-MP and the highest reduced viscosity. At the same time, it contains a high amount of sulfur.

Salts based on SPNBI-I,III were prepared under heterogeneous conditions as described in the Materials and Methods section.

TGA curves for all three SPNBIs synthesized (1–3) and K (4), Ca (5), and Cr (6) salts of SPNBI-I,III are given in Figure 3. All SPNBIs absorb moisture from the air, and the low-temperature part of the mass loss curves corresponds to its removal (Figure 3, curves 1–3). At higher temperatures of 350–400 °C, another mass loss region was observed on TGA curves of SPNBIs. As it was shown earlier [22], it is associated with desulfurization process with the formation of intermolecular –SO_2– bridging bonds. On the TGA curves of the ionomers (Figure 3, curves 4–6), a similar decomposition region is absent, which indicates the completion of the process of hydrogen replacement in the sulfo groups for metal atoms. The thermal stability of salts decreases in the cation series K > Ca > Cr, which is related to an increase in ionic radius of metal cation from potassium to calcium and then to chromium and, as a consequence, to the effect on the decomposition of the polymer salts of SPNBI-I,III. A similar pattern was observed earlier for polyphenylquinoxalines salts with alkali metals [23].

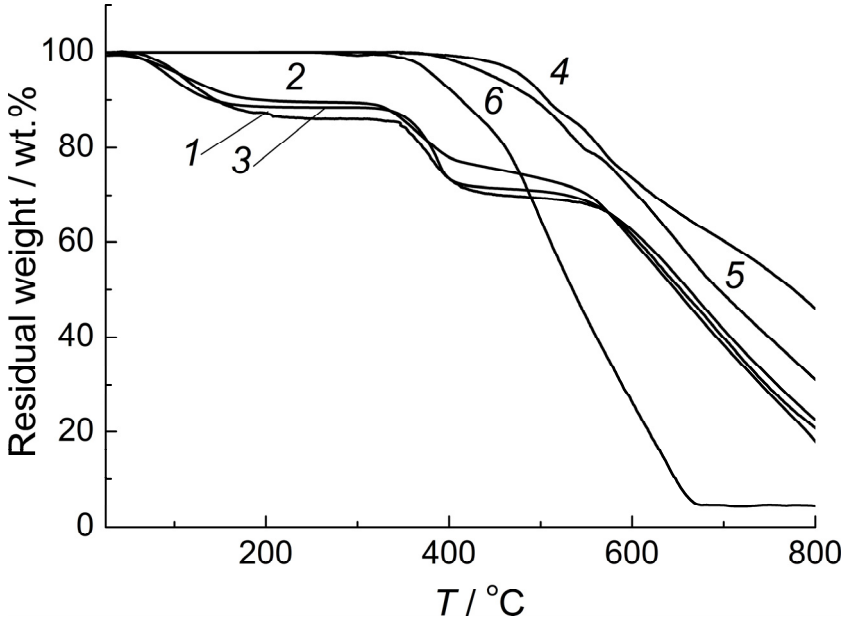


Figure 3. TGA curves for SPNBI-I,III (1), SPNBI-II,III (2), and SPNBI-II,IV (3) and K (4), Ca (5), and Cr (6) salts of SPNBI-I,III measured at a heating rate of 10 °C/min in air atmosphere.

To prepare polymer coatings on quartz crystal microbalance sensors, we used electron beam dispersion of solid polymers in vacuum (EBD) [24]. This method enables to obtain the coatings on various substrates with high adhesion and developed surface, which is necessary for sensor applications [25,26]. It should be noted that EBD allows obtaining more stable coatings than coatings obtained by aerosol method or by the dip coating or spin coating methods [10,14,27].

The properties of polymer coatings, obtained by EBD method, depend on the molecular structure of solid polymers, which are irradiated by electron beam. Electron beam heats the surface of solid polymer in vacuum and decomposes it as a result. The molecular and nanosized fragments emitted from the target polymer form the coating on the substrate surface. According to TGA data given in Figure 3, the thermal stability of various SPNBIs and the salts is different. Hence, the decomposition rates of these substances will depend on their chemical structure. This may result in different molecular structures of the coatings on the surface of QCM sensors prepared by EBD method.

Figure 4 shows the typical curve of oscillation frequency difference of the QCM sensor coated by SPNBI-I,III in water relative to the value of its oscillation frequency at the moment of its immersion in water as a function of time. It can be seen that the characteristic time (time constant) for the signal to reach a stationary level is about 1 min. The oscillation

frequency of the QCM sensors was measured when they were successively immersed into distilled water and into an acetaminophen (APAP) solution. The difference of stationary frequencies is given in Figure 5.

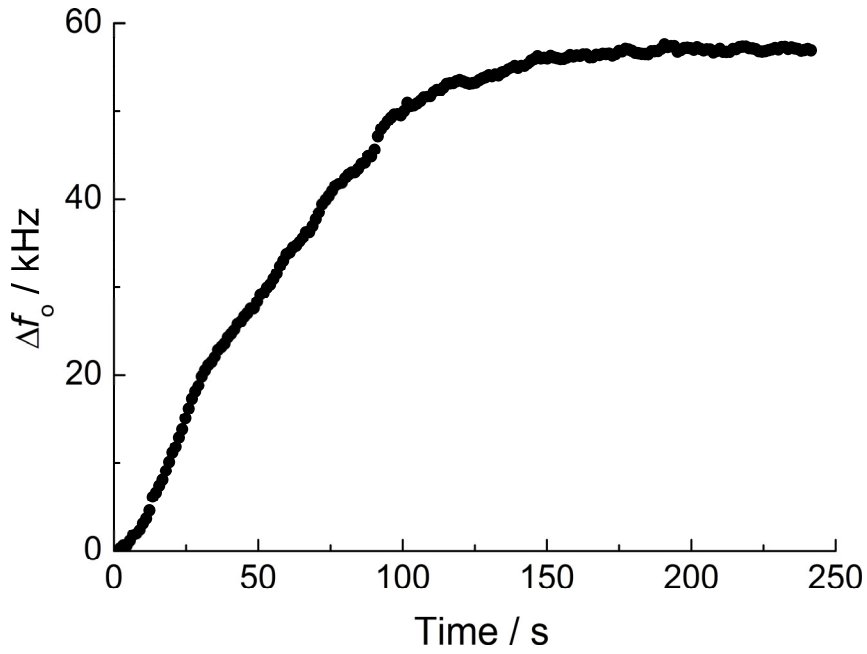


Figure 4. Typical curve of oscillation frequency difference ($\Delta f_0 = f_{\text{water}}(t) - f_{\text{water}}(0)$) of the QCM sensors coated by SPNBI-I,III immersed in water ($f_{\text{water}}(t)$) relative to the value of its oscillation frequency at the moment of its immersion in water ($f_{\text{water}}(0)$) as a function of time.

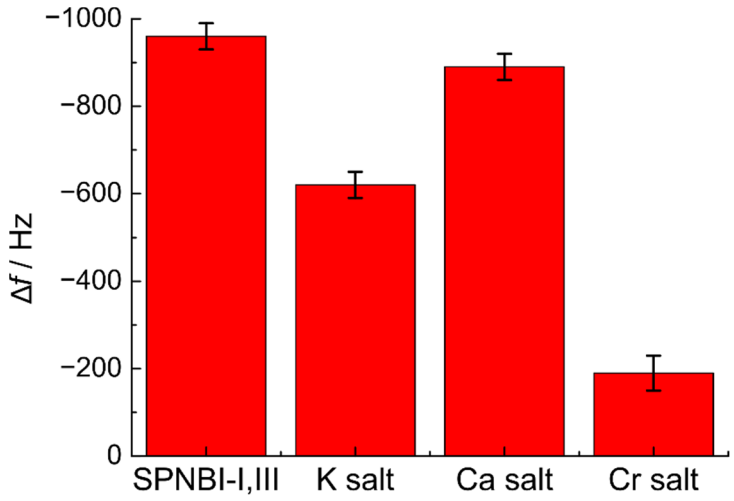


Figure 5. The oscillation frequency difference ($\Delta f = f_{\text{APAP}} - f_{\text{water}}$) between QCM sensors coated by SPNBI-I,III and its K, Ca, and Cr salts immersed in acetaminophen solution (f_{APAP}) and in distilled water (f_{water}).

As can be seen from Figure 4, the oscillation frequency of coated sensors immersed in acetaminophen solution is lower than the frequency of the same sensors immersed in distilled water. This indicates that the acetaminophen molecules in solution are adsorbed on the coating. Higher weight of resonator results in decrease of its oscillation frequency.

It should be noted that the frequencies differ markedly and statistically significantly for different coatings. This means that the response of a set of coatings to a specific substance (analyte) is characteristic.

An important issue is the relationship between sensory response and coating morphology. Atomic force microscopy (AFM) was used for morphology characterization of the coatings. Substrates for AFM from single-crystal silicon wafer as well as QCM sensors were placed in vacuum chamber and simultaneously covered by polymer coatings using EBD method. The coating thickness was calculated from the AFM images, obtained from the silicon substrates, and partly covered by mask during vacuum deposition of the coatings.

The thickness of the coatings measured by AFM is given in Figure 6.

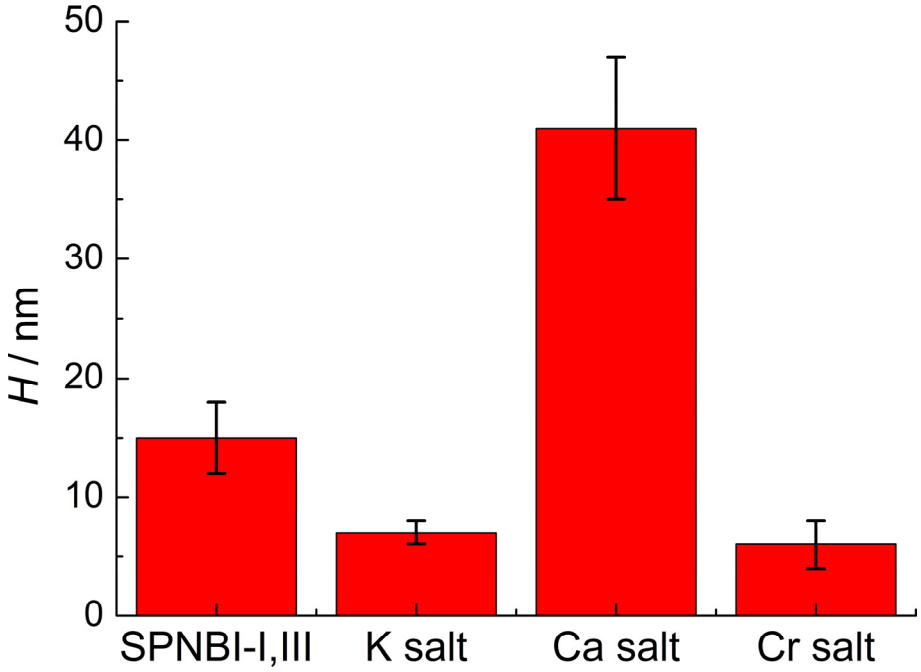


Figure 6. The thickness of the coatings (*H*) prepared from SPNBI-I,III and its K, Ca, and Cr salts by the EBD method and measured using AFM.

Comparison of the change in the frequency of QCM sensors covered by different coatings and the thickness of the coatings demonstrates that the thickness of the coating plays a significant role in the magnitude of the QCM sensor response. Coatings containing calcium have the highest sensory response. At the same time, although the coatings containing potassium and chromium have the smallest and almost equal thickness, the coatings containing potassium have a significantly higher QCM sensor response, which is almost three times greater than the one of the chromium-containing coatings. This means that both the structure of the polymer, which provides the adsorption properties of the coating, and the thickness of the coating play a role in the formation of the QCM sensors response.

The morphology of the coatings obtained using AFM is shown in Figure 7.

The morphology of the coatings shows a granular structure. The grain size depends on the type of ionomer. Coatings containing calcium have the largest grain size (~30 nm) (Figure 7c). Coatings from SPNBI-I,III and its chromium salts have the smallest grain size (10–15 nm) (Figure 7a,d). Obviously, the grain size affects the adsorption properties of coatings with respect to various analytes. The most developed surface, in accordance with the scale along the z-axis, has the coating containing calcium (Figure 7c) and the least developed one has the coating containing potassium (Figure 7b). Apparently, this makes a significant contribution to the observed difference in the adsorption capacity of the respective coatings (Figure 5).

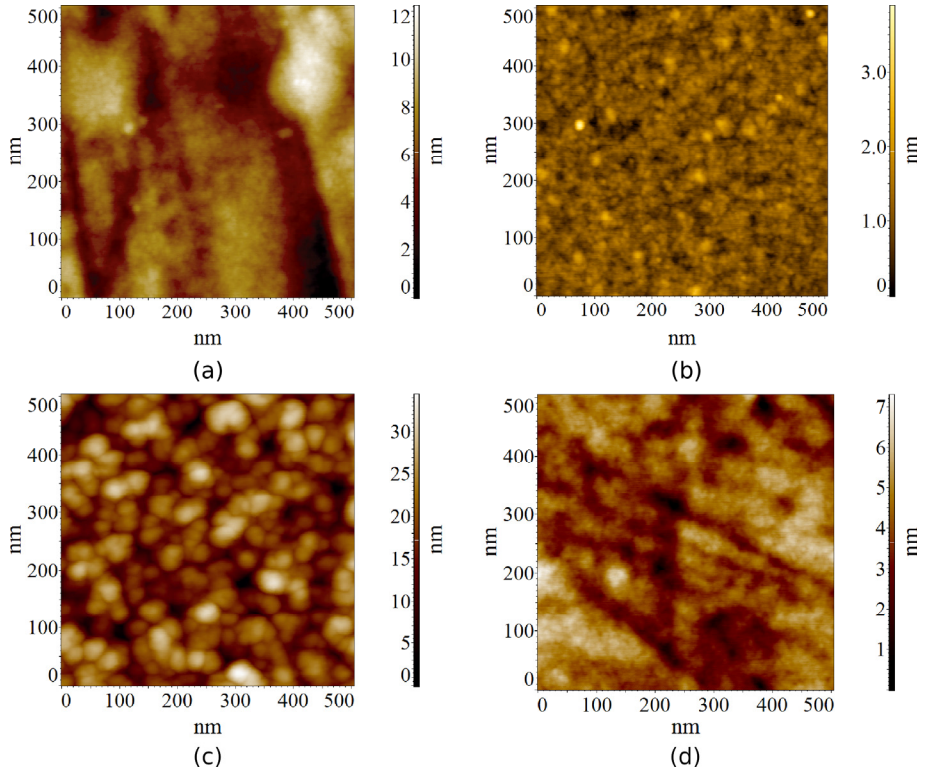


Figure 7. AFM images of the coatings prepared from SPNBI-I,III (**a**) and its K (**b**), Ca (**c**), and Cr (**d**) salts.

Thus, the data about the sensor response of QCM sensors with coatings from SPNBI and ionomers based on it, containing various metal ions, demonstrate that the suggested coatings can be used for the development of multisensor systems for recognition of specific substances in water solutions.

3. Materials and Methods

3,3′,4,4′-tetraaminodiphenyl oxide was prepared in accordance with [17]. T_m = 149–151 °C. Analysis: calculated for $C_{12}H_{14}N_4O$: C—62.59%, H—6.13%, N—24.34%. Found: C—62.53%; H—6.18%; N—23.98% (according to the literature data T_m. = 149–151 °C [17]).

1,3-Bis(3,4-diaminophenoxy)benzene was prepared according to [18]: T_m = 169–171 °C. Analysis: calculated for $C_{18}H_{19}N_4O_2$: C—67.10%, H—5.57%, N—17.34%. Found: C—66.89%, H—5.52%, N—17.36%.

1,4,5,8-Naphthalenetetracarboxylic acid dianhydride was used as anhydride, and 1,3-bis(1,8-dicarboxynaphthoyl-4)benzene dianhydride was synthesized according to the procedure described in [18]. T_m is above 360 °C. Analysis: calculated for $C_{30}H_{14}O_8$: C—73.00%, H—2.61%. Found: C—72.40%, H—2.97%.

For the synthesis of SPNBI, 6×10^{-3} mole of the corresponding bis-naphthalic dianhydride sulfuric acid (9 mL, c = 98%, d = 1.8 g/mL) was added, and the mixture was stirred until a homogeneous mass formation. For the reaction mixture, 6×10^{-3} mole of the corresponding tetraamine was added and stirred under argon flow, and then oleum (3 mL, c = 56 wt.%) was added to the mixture. The temperature of the reaction mixture was increased up to 70 °C. After the termination of the exothermic reaction, the reaction mixture was heated at 120 °C in argon atmosphere. At certain intervals, the reaction solution was poured into distilled water; the precipitated polymer was filtered off and washed with distilled water until neutral reaction. After that, the polymer was washed with acetone and dried in vacuum at 80 °C to constant weight.

To prepare salts in accordance with the previously developed procedure [6,28], SPNBI-I,III, containing 5.9 wt.% of sulfur was mixed with 10% aqueous solutions of K_2CO_3, $Ca(Ac)_2$, and $CrCl_3$, respectively. The reaction mixture was stirred for 10 days at room

temperature, the residue was repeatedly washed with water until neutral reaction, and dried at T =150 °C to constant weight. The degree of substitution of hydrogen atoms into the sulfo groups was estimated based on the amount of metal included in the polymer found by the method of flame emission spectrometry. Salts containing 8.0 wt.% of K, 4.2 wt.% of Ca, and 3.0 wt.% of Cr were prepared.

FTIR spectra were recorded for KBr pellets on a Thermo-Nicolet Nexus 670 Fourier transform IR spectrophotometer (ThermoFisher Scientific, Ramsey, MN, USA) to control the completeness of the synthesis.

Cross-polarization magic angle spinning (CP/MAS) solid state 13C NMR spectra were recorded on a Varian Unity INOVA 500 (Varian, Inc., Palo Alto, CA, USA) at 125.758 MHz. The samples were spun in a 3.2 mm rotor at 12–13 kHz. A contact time of 1.5 ms, a repetition time of 3 s, and a spectral width of 400 ppm were used for the accumulation of 1000–1500 scans. Chemical shifts were calibrated indirectly through the adamantane signal at 38.3 ppm relative to TMS.

Solution phase 13C NMR spectra were acquired using Bruker Avance AV-300 (75 MHz) spectrometer (Bruker Optik GmbH, Ettlingen, Germany) in D2SO4. Chemical shifts are reported in ppm and referenced to the tetramethylsilane.

Thermogravimetric measurements (TGA) were performed on Derivatograph-C (MOM, Budapest, Hungary) using samples having weight of about 15 mg at a heating rate of 10 °C/min in air.

To prepare polymer coatings on QCM sensors, we used electron beam dispersion of solid polymers in a vacuum (EBD) [23]. This method allows to form coatings on various substrates with high adhesion and simultaneously with a developed surface, which is necessary for sensor applications [25,26]. It should be noted that EBD makes it possible to prepare more durable coatings than coatings applied by the aerosol method or by the dip coating or spin coating methods [10,14,27].

N-acetyl-p-aminophenol (APAP, acetaminophen, paracetamol) was used as the test substance. The choice of this substance is determined by the fact that it is an important drug. Although a number of analytical methods for its analysis are available, there is a need to create a simple and cheap technique for its determination [29]. Acetaminophen is also a test substance for other methods, in particular SERS [30]. Using a set of QCM sensors with different coatings, it is possible to implement a biosensing system for diagnostics of infectious diseases [31].

Coating thickness control during deposition was carried out using STM-1 quartz microbalance (Sycon Instruments, Syracuse, NY, USA). The substrates for applying polymer coatings were quartz resonators with a resonant frequency of 10 MHz (manufactured by JSC Piezo, Moscow, Russia).

The coatings prepared were studied using atomic force microscopy (AFM) in the semi-contact mode using an NTEGRA Prima scanning probe microscope (NT-MDT Spectrum Instruments, Moscow, Russia). The signals from the QCM sensors were recorded on a setup that included a generator and an EZ Digital FC-3000 Frequency Counter (EZ Digital Co., Ltd., Nae-dong, South Korea). The resonant frequency of oscillations of quartz resonators was recorded. The measurement technique is detailed in [32].

4. Conclusions

For the first time, one-step synthesis of polynaphthoylenebenzimidazoles containing functional sulfo groups has been developed starting directly from monomers in a mixture of sulfuric acid with oleum. This method allows not only to diminish the number of reaction stages, but also to avoid the use of environmentally hazardous chemical reagents such as phenolic, amide solvents, methanol, etc., as well as to reduce energy costs. As a result, SPNBIs were synthesized in an efficient, modern, and technologically advanced way. A series of polymers was obtained, from which the optimal procedure was chosen for further research. Salts containing K, Ca, and Cr cations were prepared by polymer analogous transformations. Polymer coatings with sensor properties were deposited using

the method of electron beam dispersion of solid polymers in vacuum. These coatings were simultaneously deposited on QCM sensors and silicon wafers. Morphology study of the coatings on silicon wafers showed that coatings have granular structure, with the grain size depending on the type of ionomer. It was shown that the coatings formed from a series of polymer salts have different adsorption activity in acetaminophen–water solution compared to distilled water. The QCM results indicate that sensor signal correlates with polymer coating thickness, morphology, and its chemical composition. Thus, it was demonstrated that newly synthesized polymers may be used as the basis of a multisensor system for the detection of drugs in water solutions.

Author Contributions: Conceptualization, E.G.B., M.Y.Y. and M.I.B.; methodology, N.M.B. and G.G.N.; software, A.I.B.; validation, G.G.N., V.G.V. and A.I.B.; formal analysis, R.V.G.; investigation, N.M.B., R.S.B., R.V.G. and M.Y.Y.; data curation, V.G.V. and M.Y.Y.; writing—original draft preparation, E.G.B. and M.Y.Y.; writing—review and editing, A.I.B. and M.I.B.; supervision, M.I.B.; funding acquisition, M.I.B. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Russian Foundation for Basic Research (Project No 20-03-00348).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: Synthesis of 1,3-bis(3,4-diaminophenoxy)benzene and 1,3-bis(1,8-dicarboxynaphthoyl-4)benzene dianhydride as well as TGA measurements were performed with the financial support of the Ministry of Science and Higher Education of the Russian Federation in INEOS RAS. AFM study was supported in part by the Ministry of Science and Higher Education of the Russian Federation within the framework of the State Assignment of the Federal Research Center "Crystallography and Photonics" of the Russian Academy of Sciences using the equipment of the Center for Collective Use of the Federal Research Center "Crystallography and Photonics". The polymer coatings were prepared in ISPM RAS with the financial support of the Ministry of Science and Higher Education of the Russian Federation (Contracts FFSM-2021-0005 and FFSM-2021-0006).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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