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SYNTHESIS OF HIGH-SULFUR POLYMERS BASED ON THE TENGIZ SULFUR COPOLYMERIZATION WITH ANILINE

Abstract. The article describes the technique developed by the authors for the synthesis of high-sulfur polymers, based on the copolymerization of Tengiz sulfur with aniline. The sulfur was introduced into the reaction mixture in a colloidal form. Colloidal activated sulfur was prepared in situ from sodium polysulphides Na_2S_x, (x = 4.0-4.5), obtained from $Na_2S{\cdot}9H_2O$. Synthesis of new sulfur and aniline copolymers was carried out in the presence of oxidation systems: H_2O_2 / $FeCl_3$ / HCl, H_2O_2 / $FeSO_4$ / H_2SO_4 and $K_2Cr_2O_7$ (H_2O_2) / HCl. Depending on the reaction conditions, the nature of the oxidation system, the addition of gelatin or surfactant to the reaction mixture, sulfur-aniline polymers with a high sulfur content were obtained: from 63.8 to 89.4%. Conditions for carrying out the reaction have been found, which make it possible to vary the sulfur content of the obtained materials. The physico-chemical properties and microstructures of the obtained high-sulfur aniline-based polymers were also studied. The synthesized polymers have a high sulfur heat resistance, semiconducting properties, a developed surface morphology and are promising for the development of modern cathode active materials of rechargeable lithium power sources.

Key words: Tengiz sulfur, lithium-sulfur batteries, copolymerization, aniline, sulfur.

Introduction

The rapid growth of oil and gas production in the last decades has led to an increase in the production of petroleum sulfur, as it is a large-scale by-product of oil and gas processing. In Kazakhstan, only at the Tengiz gas processing plant, 2-3 million tons of sulfur are produced per year as a result of primary oil refining from associated components, which resulted in the accumulation of more than 10 million sulfur tons in the Tengiz field at the sulfur storage site. The inevitable consequence of this is the technogenic impact on environmental objects [1, 2]. From this perspective, the actual task is the development of modern utilization ways of Tengiz sulfur into new polymeric sulfur composites, possessing a number of valuable properties that will increase the world demand for elemental sulfur. The unique properties of sulfur and its polymer compositions, special properties of which, depending on the modifying conditions and composition of the polymer composition, led to the search for new "science intensive" technologies that ensure the economic and environmental feasibility of their application in various industries.

One of the new research areas in polymer sulfur technology is the creation of electroconductive, electrochemically active polymeric sulfur composites for use as cathode materials for lithium-sulfur batteries [3-20].

Lithium-sulfur batteries were first shown to the world public by Sion Power company in 2004. Even then, such batteries were much more efficient than current lithium-ion batteries. The main distinguishing features of these drives can be called a less expensive production, as well as more than double the increased capacity compared with the analogue. This type of battery is called Li-S. Prospectivity of lithium-sulfur current sources is due to high values of their theoretical specific energy (2500 W·h/kg), low cost and environmental safety. In terms of their energy intensity, they outperform other chemical sources of current 2.5-5 times. Overseas work on the creation of lithium-sulfur current sources intensively was conducted in the United States, South Korea, China, Japan, Russia [14-20].

Experimental

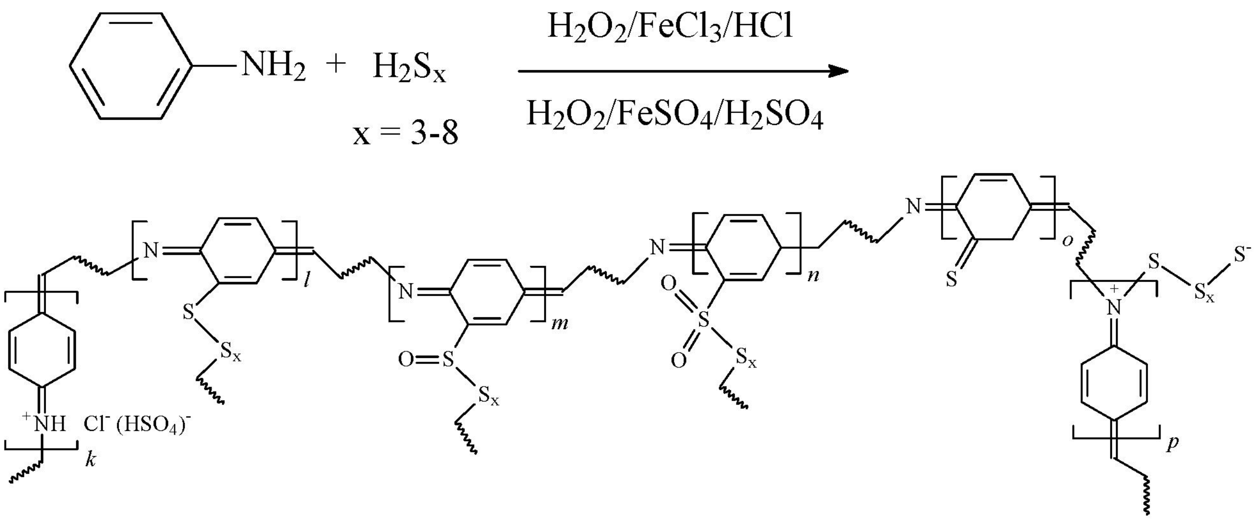
In order to develop original methods for the production of new high-sulfur polymers based on aniline and elemental sulfur (Tengizchevroil company), the work authors have studied the oxidation-reduction processes of elemental sulfur copolymerization with aniline, leading to the formation of colloidal cross-linked polymers. New high-sulfur polymers with thermal stability, electrical conductivity, developed morphological surface, promising as electrochemically active cathode materials of modern lithium batteries are obtained.

Colloidal cross-linked copolymers were synthesized by redox sulfur copolymerization with aniline. The sulfur was introduced into the reaction mixture in a colloidal form. The colloid activated sulfur was prepared by in situ from sodium polysulphides Na_2Sx, (x = 4.0-4.5), obtained from $Na_2S{\cdot}9H_2O$.

Synthesis of new sulfur and aniline copolymers was carried out in the presence of oxidation systems: H_2O_2 / $FeCl_3$ / HCl, H_2O_2 / $FeSO_4$ / H_2SO_4 (Scheme 1).

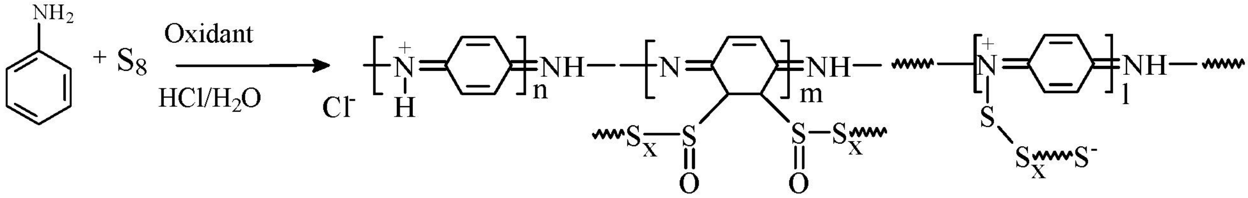
Scheme 1

$$Na_2S \cdot 9H_2O + S_x \longrightarrow H_2S_x + NaOH$$



In combination with the use of sodium polysulfides in oxidation-reduction reactions, the synthesis of high-sulfur aniline-based polymers was carried out directly by oxidation of aniline with powdered sulfur in the presence of the oxidation system $K_2Cr_2O_7$ (H_2O_2) / HCl (Scheme 2).

Scheme 2



As a result of redox copolymerization of aniline with sulfur, sulfur-aniline polymers are synthesized in the form of powders from light brown to black.

The composition of the obtained copolymers was determined by elemental analysis of the automatic analyzer «ThermoFinniganFlash EA» 1112 (Table 1).

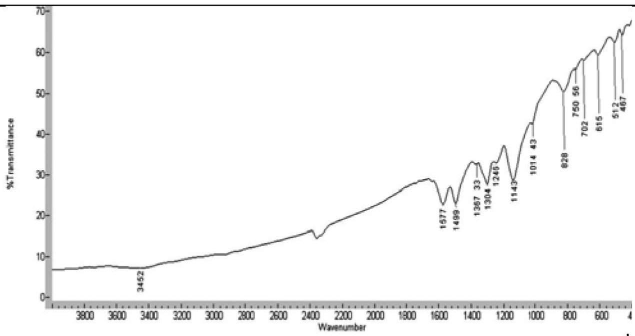
Table 1 - Element composition and melting temperature of polymers based on aniline and elemental sulfur

№	Sample cipher	Elemental analysis					$T_{melting}$, °C
		C	H	N	S	Cl	
1	An-Kz-1	9.7	0.4	1.3	80.4	-	190-240
2	An-Kz-2	10.8	0.4	1.5	82.6	1.0	122-240
3	An-Kz-3	6.8	0.4	1.2	79.5	1.1	124-240
4	An-Kz-4	8.5	0.4	1.4	89.2	0.8	165-260
5	An-Kz-5	6.7	0.3	0.7	80.2	-	120-240
6	An-Kz-6	2.1	0.1	0.3	80.2	0.6	125-260
7	An-Kz-7	2.7	0.2	0.2	89.4	-	110-120
8	An-Kz-8	5.8	0.2	0.4	87.6	-	120-220
9	An-Kz-9	4.7	0.3	0.5	84.9	-	124-230
10	An-Kz-10	2.7	0.1	0.3	63.8	-	123-230
11	An-Kz-11	6.8	0.3	0.9	78.8	7.7	124-230

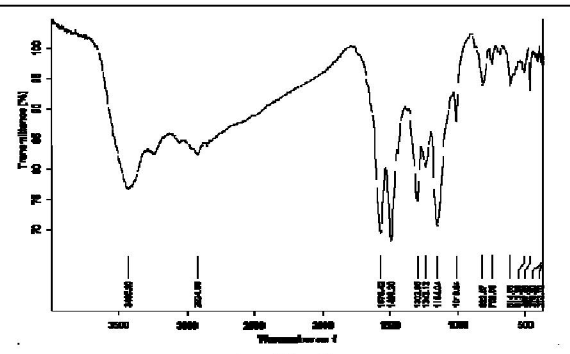
Depending on the reaction conditions, the nature of the oxidation system, the addition of gelatin or surfactant to the reaction mixture, sulfur-aniline polymers with a high sulfur content were obtained: from 63.8 to 89.4 %. The physico-chemical properties of the obtained high-sulfur aniline-based polymers were also studied. The infrared spectra of the samples were recorded on a BrukerVertex 70 spectrometer in the 400-4000 cm^{-1} region (in KBr tablets). Thermogravimetric analysis of the samples was performed on a Q-1500 derivatograph of the Paulik-Paulik-Erdei system (MOM, Hungary), the sample weight was 50 mg, the DTA sensitivity was 1/5, and the heating rate was 10 °C / min. The specific electric conductivity of the copolymers was measured on a direct current using a standard «E6-13A» terameter. The test samples were prepared in the form of tablets by pressing under a pressure of 700 kg / cm^2.

In the IR spectra of high-sulfur aniline-based polymers (Table 2), there are characteristic absorption bands (cm-1): 1578, 1498 (ν, C=C polyaniline chains); 1375 (δ, C=C-H); 1301 (ν, O=S=O); 1239 (ν, C=S, ν, C-N); 1145 (ν, O=S=O); 1014 (ν, O=S); 883, 826 (δ, C=C-H); 618, 582, 506 (ν, C-S); 468 (ν, S-S).

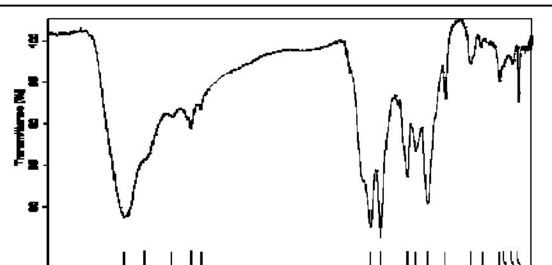
Table 2 - IR spectra of high-sulfur aniline-based polymers



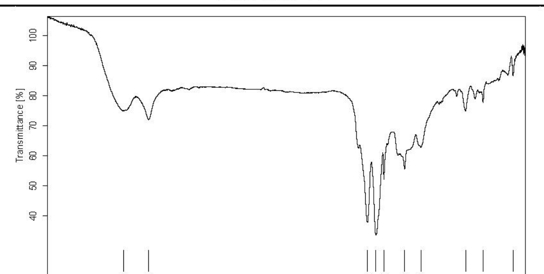
An-Kz-1



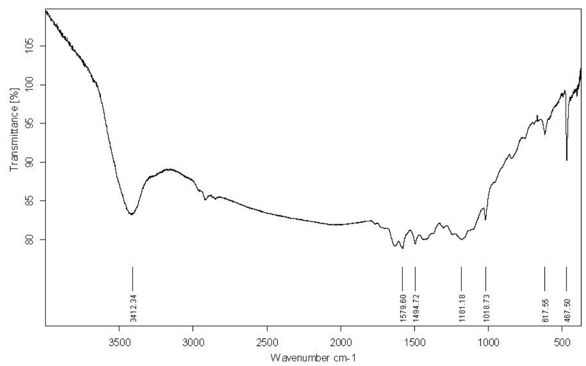
An-Kz-2



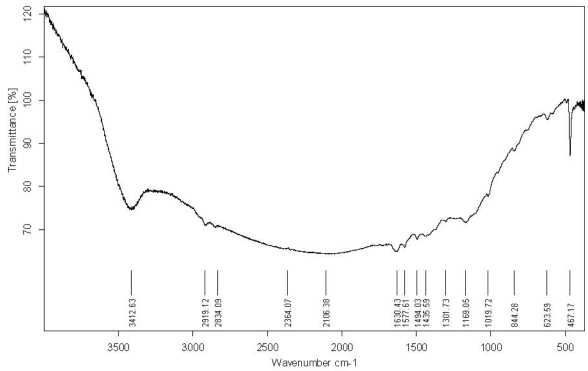
An-Kz-3



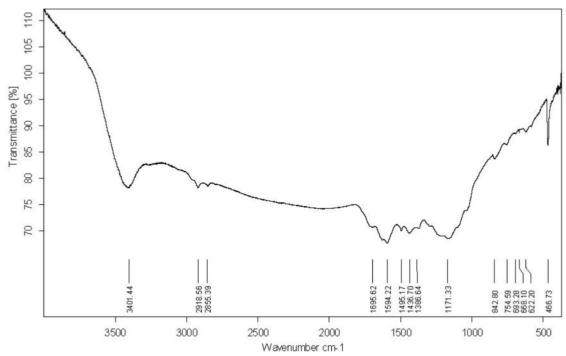
An-Kz-5



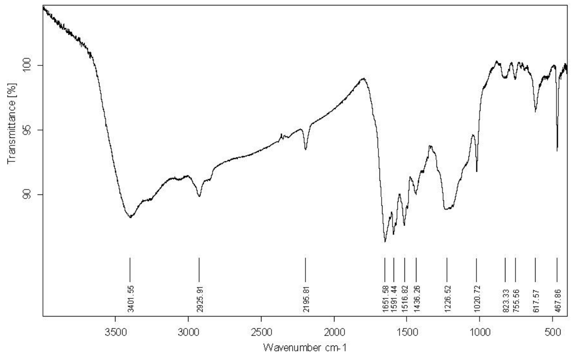
An-Kz-6



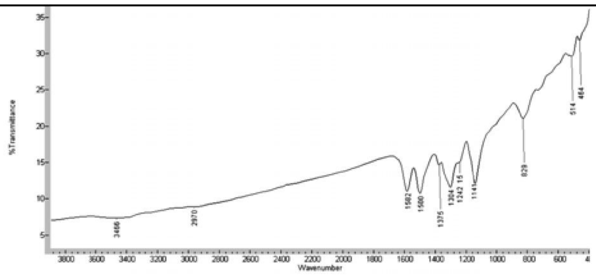
An-Kz-7



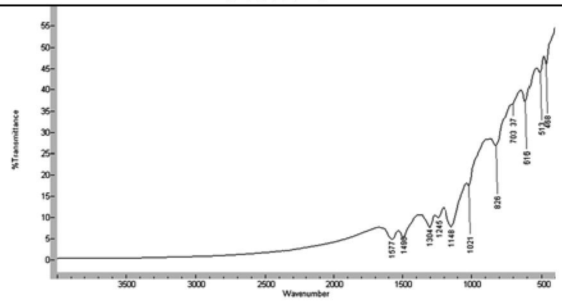
An-Kz-8



An-Kz-9



An-Kz-10



An-Kz-11

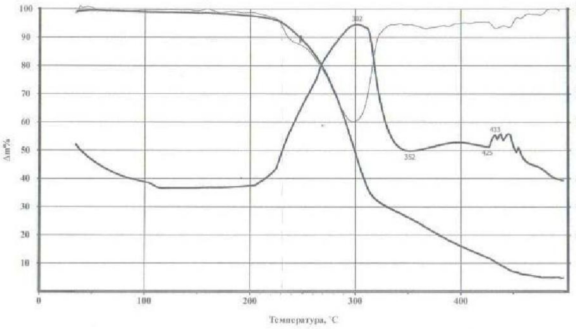
When studying the electrical conductivity of the obtained high-sulfur aniline-based polymers, it was found that they have a specific electrical conductivity of the 10^{-6}-10^{-13} S / cm order, corresponding to high-resistance organic semiconductors (Table 3).

Table 3 - Specific electrical conductivity (σ) and thermogravimetric analysis data of high-sulfur aniline-based polymers

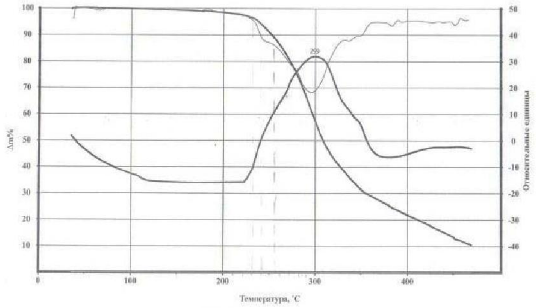
№	Sample cipher	S content, %	The onset temperature of the thermooxidative degradation, °C	σ, S/cm
1	An-Kz-1	80.39	~210	$8.1 \cdot 10^{-6}$
2	An-Kz-2	82.58	~230	$7.4 \cdot 10^{-6}$
3	An-Kz-3	79.47	~220	$9.1 \cdot 10^{-8}$
4	An-Kz-4	89.20	~210	1.2·10-7
5	An-Kz-5	80.19	~230	$2.3 \cdot 10^{-7}$
6	An-Kz-6	80.23	~220	$2.5 \cdot 10^{-14}$
7	An-Kz-7	89.35	~230	$4.2 \cdot 10^{-13}$
8	An-Kz-8	87.59	~230	$5.6 \cdot 10^{-12}$
9	An-Kz-9	84.93	~220	$4.8 \cdot 10^{-13}$
10	An-Kz-10	63.78	~220	$5.1 \cdot 10^{-7}$

According to the results of thermogravimetric analysis, the polymers obtained have a high resistance to thermal-oxidative degradation (up to 210-230 °C) (Table 3, 4).

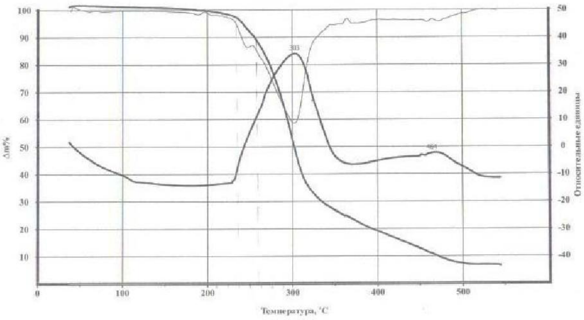
Table 4 - Curves of thermogravimetric analysis of high-sulfur aniline-based polymers



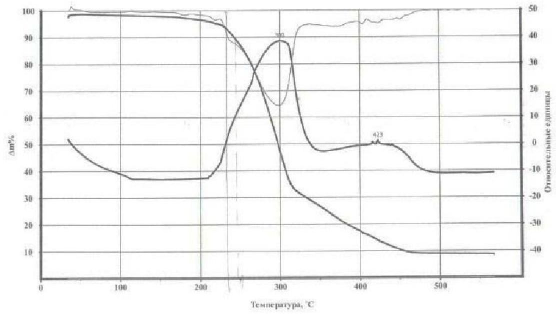
An-Kz-1



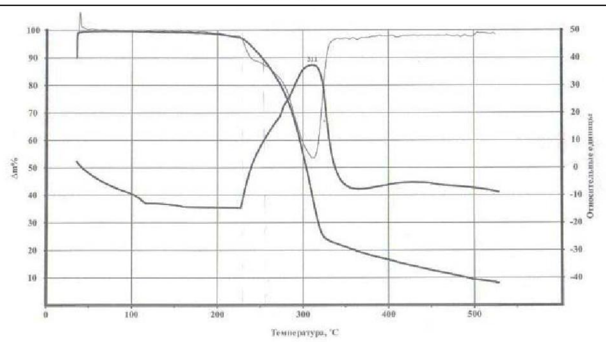
An-Kz-2



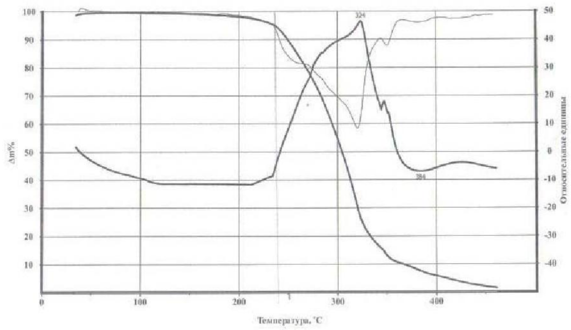
An-Kz-3



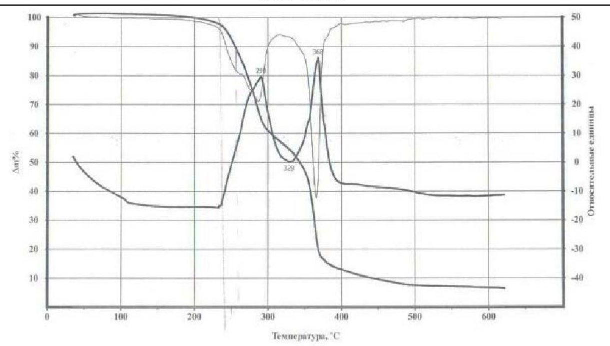
An-Kz-4



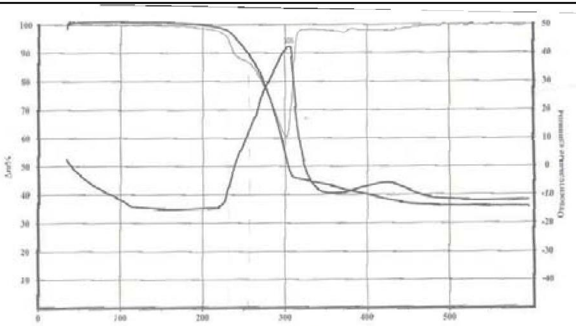
An-Kz-5



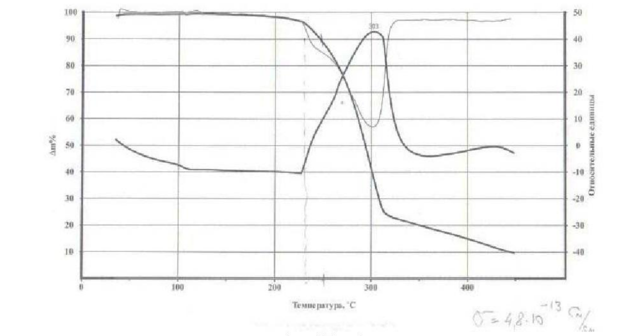
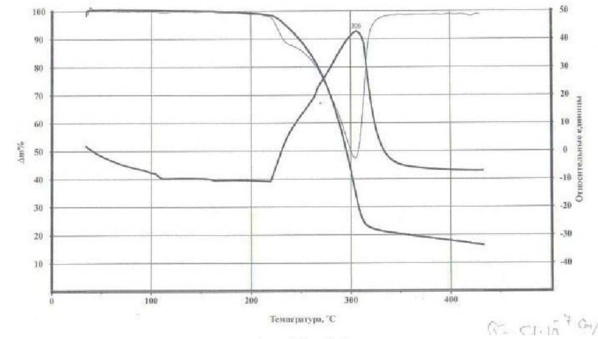
An-Kz-6



An-Kz-7



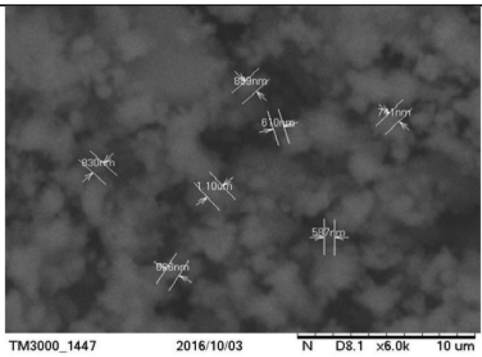
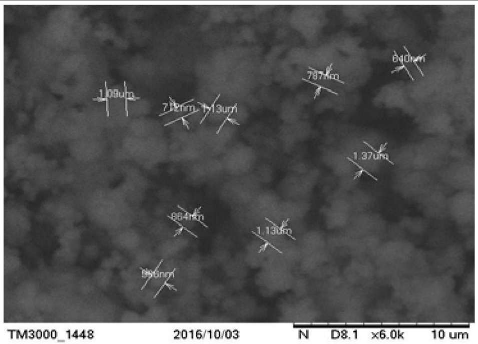
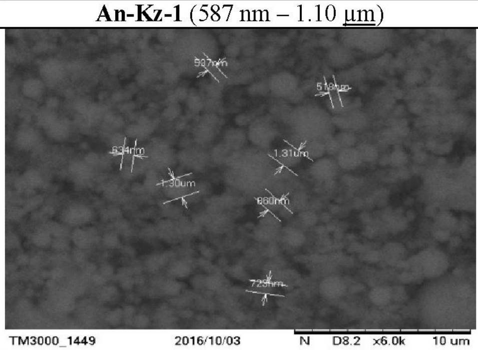
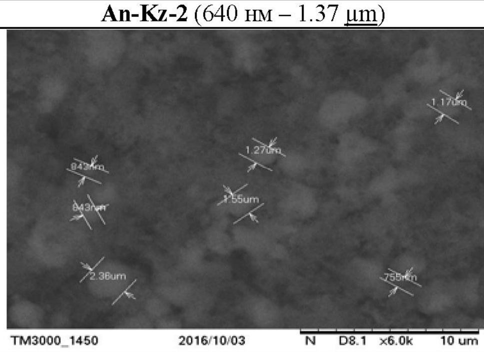
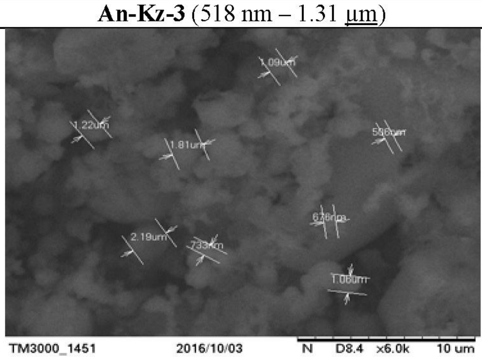
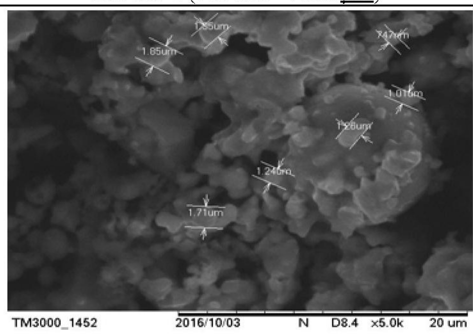
An-Kz-8

	
An-Kz-9	An-Kz-10

In order to perform comparative studies of the high-synthesized polymers microstructure based on aniline used X-ray dispersive spectral microanalysis method using an electronic microscope TM 3000 Hitachi.

Typical micrographs of the obtained high-sulfur copolymers are shown in Table 5.

Table 5 - Micrographs of high-sulfur aniline-based polymers

	
An-Kz-1 (587 nm – 1.10 µm)	**An-Kz-2** (640 нм – 1.37 µm)
	
An-Kz-3 (518 nm – 1.31 µm)	**An-Kz-4** (755 nm – 2.36 µm)
	
An-Kz-6 (506 nm – 2.19 µm)	**An-Kz-7** (747 nm – 1.95 µm)

The obtained results indicate that the synthesized copolymers have a developed microstructure, with rather small sizes of narrow polydispersity microparticles. The An-Kz-1 copolymer is characterized by the smallest particle sizes in the range of 587 nm to 1.10 μm. Almost the same particle sizes, copolymers An-Kz-2, An-Kz-3 and An-Kz-7 were obtained. Somewhat larger than the particle (up to 755 nm - 2.36 μm) are formed in the synthesis of an aniline-sulfur An-Kz-4 copolymer using the $H_2O_2/FeCl_3$ /HCl oxidation system and the addition of gelatin to the reaction mixture.

Conclusion

Technological methods for the synthesis of high-sulfur polymers based on the elemental sulfur redox copolymerization with aniline have been developed. Conditions for carrying out the reaction have been found, which make it possible to vary the sulfur content of the obtained materials. It has been established that synthesized high-sulfur polymers have thermal stability, semiconductor properties, developed surface morphology and are promising for the development of active cathode materials of modern rechargeable lithium current sources.

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СИНТЕЗ ВЫСОКОСЕРНИСТЫХ ПОЛИМЕРОВ, ОСНОВАННЫЙ НА СОПОЛИМЕРИЗАЦИИ ТЕНГИЗКОЙ СЕРЫ С АНИЛИНОМ

Аннотация. В статье описывается разработанная авторами методика синтеза высокосернистых полимеров, основанная на сополимеризации Тенгизской серы с анилином. Серу вводили в реакционную смесь в коллоидной форме. Коллоидную активированную серу получали in situ из полисульфидов натрия Na_2Sx, (x=4.0-4.5), полученного из $Na_2S{\cdot}9H2O$. Синтез новых сополимеров серы и анилина осуществляли в присутствии окислительных систем: $H_2O_2/FeCl_3/HCl$, $H_2O_2/FeSO_4/H_2SO_4$ и $K_2Cr_2O_7$ $(H_2O_2)/HCl$. В зависимости от условий реакции, природы окислительной системы, добавления в реакционную смесь желатина или ПАВ получены серо-анилиновые полимеры с высоким содержанием серы: от 63.8 до 89.4%. Найдены условия проведения реакции, позволяющие варьировать содержание серы в полученных материалах. Были также изучены физико-химические свойства и микроструктуры полученных высокосернистых полимеров на основе анилина. Установлено, что синтезированные высокосернистые полимеры обладают термостойкостью, полупроводниковыми свойствами, развитой поверхностной морфологией и являются перспективными для разработки активных катодных материалов современных перезаряжаемых литиевых источников тока.

Ключевые слова: Тенгизкая сера, литий-серные батарей, сополимеризация, сера, анилин

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ТЕҢІЗ КҮКІРТІ МЕН АНИЛИНДІ СОПОЛИМЕРЛЕУ НЕГІЗІНДЕ ЖОҒАРЫКҮКІРТТІ ПОЛИМЕРЛЕРДІ СИНТЕЗДЕУ

Аннотация. Бұл мақалада авторлардың құрастырған, Теңіз күкірті мен анилиннің сополимерлеуіне негізделген, жоғарыкүкіртті полимерлерді синтездеу әдістері суреттеледі. Күкіртті реакциялық қоспаға коллоидты түрде енгізеді. Коллоидты активтенген күкіртті in situ әдісі арқылы $Na_2S{\cdot}9H2O$ алынған натрий полисульфидінен Na_2Sx, (x=4.0-4.5) алды. Анилин мен күкірттің жаңа сополимерлерін алудағы синтезін келесідей қышқылдық жүйеде іске асырды: $H_2O_2/FeCl_3/HCl$, $H_2O_2/FeSO_4/H_2SO_4$ және $K_2Cr_2O_7$ $(H_2O_2)/HCl$. Реакция шарттары мен қышқылдық жүйенің табиғатына қарай, реакциялық қоспаға желатин немесе ПАВ қосу арқылы жоғары құрамды күкірті бар күкірт-анилинді полимерлер алынды: 63.8% бастап 89.4% дейін. Алынған материалдардан күкірт құрамын реттеп отыратын реакцияның жүру шарттары анықталды. Сонымен қатар, анилин негізіндегі алынған жоғарыкүкіртті полимерлердің физика-химиялық қасиеттері мен микроқұрылысы зерттелді. Синтезделген жоғарыкүкіртті полимерлер жылуға төзімділік пен жартылай өткізгіштік қасиеттерге, дамыған беттік морфологияға ие екені, және белсенді катодты материалдарын - жаңа заманғы қайта зарядталушы литийлі ток көздерін құрастыруға келешегі зоры анықталды.