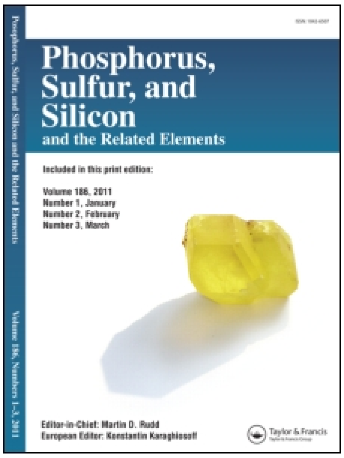

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ETHYNETHIOL-BASED POLYENEPOLYSULFIDES FROM ACETYLENE AND ELEMENTAL SULFUR: SYNTHESIS AND PROPERTIES

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ETHYNETHIOL-BASED POLYENEPOLYSULFIDES FROM ACETYLENE AND ELEMENTAL SULFUR: SYNTHESIS AND PROPERTIES

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Ethynethiol-based polysulfide polymers [$C_2H_2S_x$] (x = 1-6) have been synthesized by the reaction of sodium acetylides and elemental sulfur in liquid ammonia with the following hydrolysis of sodium ethynethiolates and spontaneous polymerization of ethynethiols thus formed. The polymers are brown powders (up to 87% sulfur content), possessing electroconducting (10^{-13}–10^{-14} $S \cdot cm^{-1}$), paramagnetic (10^{18} $spin \cdot g^{-1}$) and redox properties. Application of the polymers as active cathode materials provides for a stable cycling of model lithium batteries.

Keywords: Acetylene; elemental sulfur; ethynethiol; ethynehydropolysulfanes; lithium battery; polymers

Polysulfide polymers (thiokols) are widely used[1–5] as special rubbers, hermetics, mastics, compositions, pigments, and so on. Such polymers are commonly prepared by polycondensation of aliphatic and aromatic dihalogen compounds with sodium polysulfides,[3,4] or by copolymerization of sulfur with unsaturated hydrocarbons.[1,5] Over the last decade, investigations on the development of new lithium-sulfur rechargeable batteries have drawn attention to high sulfur content redox active polymers as potential active components of cathode compositions.[6–19] Among these, of a special interest, are electroconductive polymers, since, theoretically, they should improve transfer of electrons to the outer circuit.

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Recently, we undertook a systematic investigation on deep sulfurization of polymers (polysiloxanes,[14] polyethylene,[15,16] polystyrene,[17] polyvinylpyridine[18,19]) with elemental sulfur. As a result, new high sulfur content polymers with fused thienothiophene,[15,16] benzothiophene,[17] polythienopyridine,[18,19] polythienoazepine[18,19] structures and blocks, containing polysulfide bonds and thiokol functions, possessing electroconductivity and paramagnetism, have been prepared.

A disadvantage of the known polysulfide cathode materials is their fragmentation and formation of insoluble lithium sulfide upon reduction (discharge) and, consequently, assembly of macromolecules of different structure upon oxidation (charge). This decreases the battery discharge capacity and worsens its cyclability. Therefore, the search for electroconducting polymers with thiol, thione, and polysulfide functions, whose redox transformations would not destroy the main polymer chain, seems reasonable. Such polymers may include the polyacetylene blocks with thiol and polysulfide side groups. Approaches to the synthesis of such polymers, based on polymerization and polymer analogous transformations of acetylenic sulfides, are known.[7,9,10]

In the present work we report on a more straightforward and simple route to such polymers, involving preparation of sodium ethynethiolates in liquid ammonia from sodium acetylides and elemental sulfur followed by the hydrolysis and spontaneous polymerization of ethynethiols and their polysulfur analogs, ethynehydropolysulfanes.[20,21]

Condensation of acetylene with sulfur in aromatic amines was reported[22,23] to give perthiooxalic acid, HSC(S)C(S)SH. The properties of this compound,[24] as well as those for polymers with elementary unit [-SC(S)C(S)S-]$_n$[25] were later described. Additionally, in patents,[12,13] we briefly mentioned spontaneous polymerization of ethynemonothiols and ethynedithiols, generated in situ from acetylene and sulfur in liquid ammonia in the presence of sodium amide. Here we present and discuss experimental details concerning the synthesis of such polymers.

RESULTS AND DISCUSSION

Preparation of poly(ethynethiol) involves the following steps: first, interaction of sodium acetylide with elemental sulfur in liquid ammonia affords sodium ethynethiolate **1**.[20,21] Subsequent treatment of the reaction mixture (after removal of 2/3 ammonia volume) with 10% aqueous ammonium chloride to pH of 4–5 (see Experimental and Table I, experiments 1–3, 6) or with 10% aqueous ammonium chloride and 10%

TABLE I Preparation Conditions, Yields and Characteristics of Polysulfides

Exp. no.	Na:S ratio, g-atom	Yield (%)	m.p. (°C)	Found, S (%)	Elementary unit	Calculated, S (%)
1[a]	1:1	48.3	118–120	67.5	$C_2H_2S_2$	69.6
2[a]	1:1	30.0	96–98	55.3	C_2H_2S	55.2
3[a]	1:1	41.4	120–124	56.1	C_2H_2S	55.2
4[b]	1:2	50.0	118–120	84.1	$C_2H_4S_4$	83.1
5[b]	1:3	79.0	120–122	87.9	$C_4H_2S_6$	88.1
6[a]	1:4	63.0	119–120	84.6	$C_2H_4S_4$	83.1

[a] Quenching with 10% aqueous solution of NH_4Cl (pH ~ 4–5).

[b] Quenching with 10% aqueous solution of NH_4Cl and 10% aqueous solution of HCl (pH ~ 2–3).

aqueous HCl to pH ~2–3 (experiments 4–5) gives ethynethiol **2**.

$$HC{\equiv}CH \xrightarrow{Na/NH_3} HC{\equiv}CNa \xrightarrow{1/8S_8} \underset{\mathbf{1}}{HC{\equiv}CSNa}$$

Ethynethiol **2** thus formed, being unstable, instantaneously polymerizes, presumably mainly in the form of its most stable tautomer, thioketene **3**,* to form polythione **4**, which, seemingly, exists mainly as polyvinylenethiol **5**.[26,27] The latter may undergo intramolecular oxidation in air to form dithiolene blocks or units (structure **6**), or intermolecular oxidation resulting in disulfide cross-linking of polyvinylene chains (structure **7**). The real structure of the polymer formed may include units or blocks due to participation of the C=S group in polymerization (structure **8**) and polyaddition (structure **9**) (Scheme 1).

In fact, the composition of the polymers formed may be even more complex as it is unlikely that the successive cleavage of cyclooctasulfane S_8 with sodium acetylide gives a single product, sodium ethynethiolate **1**. Apparently, the reaction mixture should contain some amounts of sodium derivatives of all possible ethynehydropolysulfanes $HC{\equiv}CS_xNa$ ($x = 1$–8) **1, 1a–g** and diethynylpolysulfides **10a–h** $(HC{\equiv}C)_2S_x$ ($x = 1$–7) in ratio determined by the reaction conditions and reactant ratio.

$$HC{\equiv}CNa + S_8 \longrightarrow \underset{\mathbf{1}}{HC{\equiv}CSNa} + \underset{\mathbf{1a}}{HC{\equiv}CS_2Na} + \underset{\mathbf{1b}}{HC{\equiv}CS_3Na} + \underset{\mathbf{1c}}{HC{\equiv}CS_4Na} +$$

$$\underset{\mathbf{1d}}{HC{\equiv}CS_5Na} + \underset{\mathbf{1e}}{HC{\equiv}CS_6Na} + \underset{\mathbf{1f}}{HC{\equiv}CS_7Na} + \underset{\mathbf{1g}}{HC{\equiv}CS_8Na} + \underset{\mathbf{10a\text{–}h}}{HC{\equiv}CS_xC{\equiv}CH}$$

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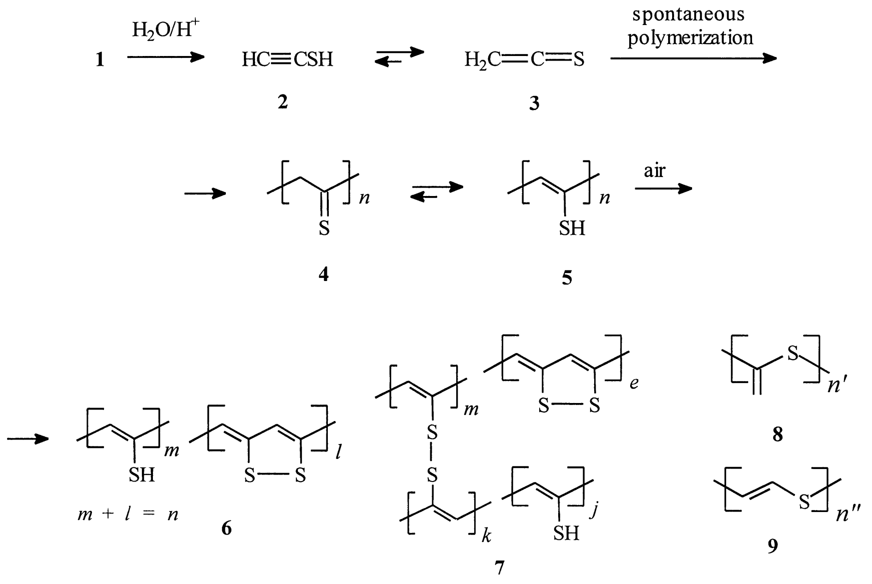
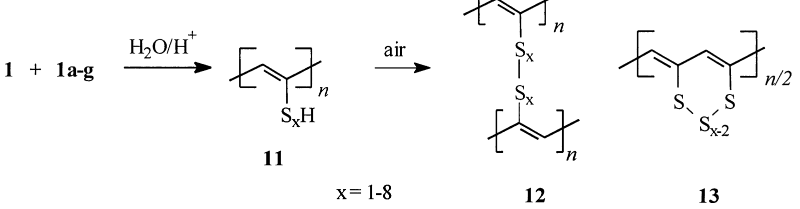
*Relative thermodynamic stability of isomers **2** and **3** evaluated by HF/6-31G(d,p) method (Yu. L. Frolov et al.) indicates a higher stability of the structure **3** (these results will be published separately).



SCHEME 1

Obviously, stability of the S—S bond in the ethynehydropolysulfanes towards cleavage under the action of the ethynide anion will increase upon shortening of the polysulfide chain due to approaching of the anion negative charge to the reaction center. Thus, the concentration of di-, tri-, and tetrasulfanes **1a–1c** may become rather high and, correspondingly, contribution of polymeric blocks of type $[-HC=C(S_xH)-]_n$ **11** and their oxidized cross-linked **12** and non-cross-linked (cyclic and macrocyclic) forms **13** to the general macromolecule structure will be significant (Scheme 2).



SCHEME 2

To check these conclusions we have attempted to detect the initially formed sodium derivatives of ethynehydropolysulfanes $HC{\equiv}CS_xNa$

($x = 1$–8) **1–1a–g** as the corresponding methylethynylpolysulfides. For this purpose, a three-fold excess of methyl iodide (relative to Na taken) was added to the reaction mixture after 3 h of stirring. After the treatment (see Experimental), a solution of the reaction mixture in $CDCl_3$ was analyzed by ^1H NMR. It is known[28] that peaks of SCH_3 group protons for compounds $RC{\equiv}CSCH_3$ (R = Me, Et, *t*-Bu) are located in the 2.28–2.33 ppm region. In 1,2-di(methylthio)ethyne ($CH_3SC{\equiv}CSCH_3$) synthesized for comparison purposes by the method,[29] the peaks of methylthio group protons are observed at 2.35 ppm ($CDCl_3$). ^1H NMR spectrum of the prepared methylated reaction mixture shows a singlet at 2.38 ppm which is attributable to the protons of the $C{\equiv}CSCH_3$ group. Along with this peak, there are several unresolved peaks of lower intensity in the 2.00–2.35 ppm region, which may be assigned to the protons of the $C{\equiv}CS_xCH_3$ ($x = 2$, 3, and so on) groups.

In fact, polymers prepared using an equimolar Na:S ratio contain ~67.5% (experiment 1), 55.3% (experiment 2) and 56.1% (experiment 3) of sulfur, that corresponds to the average elementary units $C_2H_2S_2$ (S 69.6%) and C_2H_2S (S 55.2%), instead of the expected C_4H_2S. Increasing of the Na:S molar ratio from 1:1 to 1:4 results in polymers in which the sulfur content reaches 84.1% [experiment 4 (Na:S, 1:2)], 87.9% [experiment 5 (Na:S, 1:3)], 84.6% [experiment 6 (Na:S, 1:4)], that corresponds to the average elementary units $C_2H_2S_4$ (S 83.1%) and $C_2H_2S_6$ (S 88.1%).

Since the polymer yields under conditions of experiments 1–6 are ~30–79% (relative to Na employed), one may suggest that either the reaction is incomplete and sodium acetylide remains unreacted or sodium is partially consumed to form water soluble sodium polysulfides.

The polymers obtained in experiments 1-6 are brown powders with m.p. of 96 to 124°C. They are limitedly soluble in organic solvents (ether, benzene, chloroform, acetone).

The polymer from experiment 3 (S 56.1%, m.p. 120–124°C) was fractionated with benzene in a Soxhlet apparatus (5 h) to give two fractions: benzene-insoluble residue 3a (S 52.3%, m.p. 138–140°C) and benzene-soluble part 3b (S 59.1%, m.p. 89–92°C).

The ^1H NMR spectrum ($CDCl_3$) of fraction 3b shows several groups of unresolved multiplets in the 5.17–5.20, 5.99–6.04, 6.90–7.11, 7.78 ppm regions, which may be attributed to the protons adjacent to the double bond in different structural fragments (Schemes 1 and 2).

In the IR spectra (KBr) of the synthesized polysulfides (Table II) there are broad indistinct absorption bands typical for polymeric products. Thus, in the 1580–1300 cm^{-1} region, an intense broad weakly resolved band with maxima at 1579–1510, 1460–1450,

TABLE II IR Spectra of Polysulfides (KBr)

Exp. no.	IR spectra, cm^{-1}
2	2970 vw, 2916 vw (ν, C=H); 1510 w, 1450 s, 1370 w (ν, C=C); 1282 s, 1130 (ν, C=S); 1080 w [δ, C=C(S)S]; 992 vw, 937 vw [δ, H—C(HS)=C]; 790 w, 675 w, 543 w (ν, C—S); 490 vw (ν, S—S)
3	3059 vw, 2957 vw, 2919 vw (ν, C—H); 1557 w, 1520 w, 1460 s, 1367 w, 1315 w (ν, C=C); 1278 s, 1203 w, 1141 w (ν, C=S); 1080 w, 1020 w [δ, C=C(S)S]; 993 vw, 965 w, 909 w [δ, H—C(HS)=C]; 809 w, 762 w, 728 w, 668 w, 648 w, 544 w, 520 vw (ν, C—S); 487 vw (ν, S—S)
3a	3059 vw, 2908 vw, 2841 vw (ν, C—H); 1576 w, 1543 w, 1515 w, 1456 s, 1418 m, 1372 w (ν, C=C); 1280 w, 1254 w, 1200 w, 1144 w (ν, C=S); 1068 w, 1020 w [δ, C=C(S)S]; 970 w, 904 w [δ, H—C(HS)=C]; 827 w, 789 w, 733 w, 680 w, 523 w (ν, C—S); 420 w (ν, S—S)
3b	3057 vw, 2957 vw, 2915 w, 2855 vw (ν, C—H); 1579 w, 1567 w, 1548 w, 1523 w, 1459 s, 1418 sh, 1369 w (ν, C=C); 1274 m, 1254 w, 1193 w, 1139 w (ν, C=S); 1079 w, 1067 w [δ, C=C(S)S]; 994 w, 901 w [δ, H—C(HS)=C]; 807 w, 789 w, 752 w, 726 w, 668 w, 646 w, 546 vw (ν, C—S); 485 w (ν, S—S)
5	2957 vw, 2909 vw, 2840 vw (ν, C—H); 1560 w, 1459 s, 1418-1367 a broad band with three maxima, 1305 w (ν, C=C); 1203 w, 1140 w (ν, C=S); 1080 m, 1020 w [δ, C=C(S)S]; 965 w, 902 w [δ, H—C(HS)=C]; 800 w, 762 w, 710 w, 650 w, 600 w, 535 w (ν, C—S); 460 w (ν, S—S)

1418–1410, 1372–1367 cm^{-1}, which correspond to the vibrations of polyenepolythiol, polyenepolysulfide, polyenedithiolene moieties in structures **5–7**, **9**, **11–13** (Schemes 1 and 2),[14–18,30,31] is observed. In the 1300–1100 cm^{-1} region there are three absorption bands: 1282–1254, 1213–1190, and 1144–1130 cm^{-1}, assignable to the stretching vibrations of the C=S group in structures of type **4**.[31–34] Absorption bands in the 1080–1020 cm^{-1} region presumably belong to the deformations of the C=C—S groups in structures of types **6–9**, **12**, **13**.[31] According to Kazitsina and Kupletskaya,[35] weakly resolved absorption bands at 995–901 cm^{-1} may correspond to the deformations of H—C(HS)=C groups in structures **5**, **6**, **11**. Weak indistinct maxima at 827–800, 790–710, 680–600, 546–520 cm^{-1} are likely to belong (according to Lozach,[34] Kazitsina and Kupleskaya,[35] Nakanishi,[36] and Trofimov and Amosova[37]) to the stretching of the C—S bonds in various polymeric structural units, and also to the deformations vibrations of the C—H bonds.[38] In all the polymers, weakly intense peaks in the 490–420 cm^{-1} region are observed. This absorption may be related[32,34–36] to the S—S bond vibrations in the dithiolene blocks and di- and polysulfide moieties in structures **6**, **7**, **12**, **13**. The weak absorptions in the 3059, 2970–2957, 2919–2907, 2855–2840 cm^{-1} regions correspond to the stretchings of residual C—H groups.

Electroconductivity, paramagnetism and electrochemical activity of the polyenepolysulfide from the experiment 3 (S 56.1%) and its fractions 3a (S 52.3%) and 3b (S 59.1%) have been investigated.

ESR spectra of polymers 3a and 3b show asymmetric narrow signals ($\Delta H = 0.9$–1.1 mT, $g \approx 2.008$), corresponding to the paramagnetic center concentration of ca 10^{18} $\text{spin} \cdot \text{g}^{-1}$. Character of the signals allows one to assign them to the sulfur-containing polymeric conjugated structures. The expressed asymmetry is likely to be associated with superposition of signals caused by the presence of several types of paramagnetic polysulfide conjugated structures (like **6**, **11**) in the samples studied.

The polyenepolysulfide (from experiment 3) and its fractions 3a and 3b possess electroconductivity of $2.7 \cdot 10^{-14}$, $1.3 \cdot 10^{-14}$ and $4.2 \cdot 10^{-13}$ $\text{S} \cdot \text{cm}^{-1}$ respectively. Higher electroconductivity of the polymer 3b, as well as its solubility in benzene indicate a more regular structure of this polymer.

Redox behavior and electrochemical activity of the polymers were studied in potentiodynamic and galvanostatic modes. Shapes of cyclic voltammograms for the studied samples (Figure 1) resemble those for compounds containing polysulfide units. In the potential range of 1.25–3.00 V, a complex multistage process of the polymers reduction with the maxima at 2.40, 2.10, 1.96 and 1.80 V is observed. Subsequent oxidation proceeds in two stages with the maxima at 2.36 and 2.54 V. Locations of the cathode and anode maxima, as well as amplitudes of the oxidation

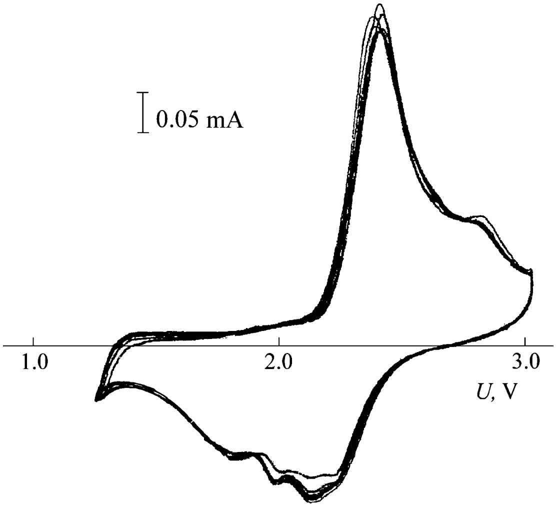


FIGURE 1 Cyclic voltammogram of polyenepolysulfide (experiment 3, S = 56.1%) for second to tenth cycles. Potential scan rate is $1 \text{ mV} \cdot \text{s}^{-1}$ (vs. Li^+/Li).

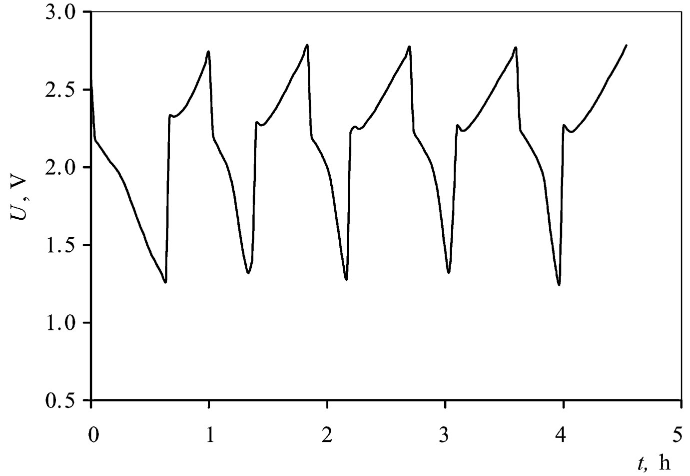


FIGURE 2 Cyclic chronopotentiogram of a cathode based on the polyenepolysulfide (experiment 3) for first to fifth cycles (a model lithium cell).

and reduction currents remain almost unchanged upon prolonged (up to 10 cycles) cycling.

The discharge curves for first to fifth cycles (Figure 2) illustrate stable cycling of a model lithium cell cathode based on the non-fractionated polyenepolysulfide (experiment 3) in the potential range of 1.25–2.80 V.

Chronopotentiograms of the first discharge cycle for cathodes based on the net polymer (experiment 3) and its soluble fraction (3b) (Figure 3)

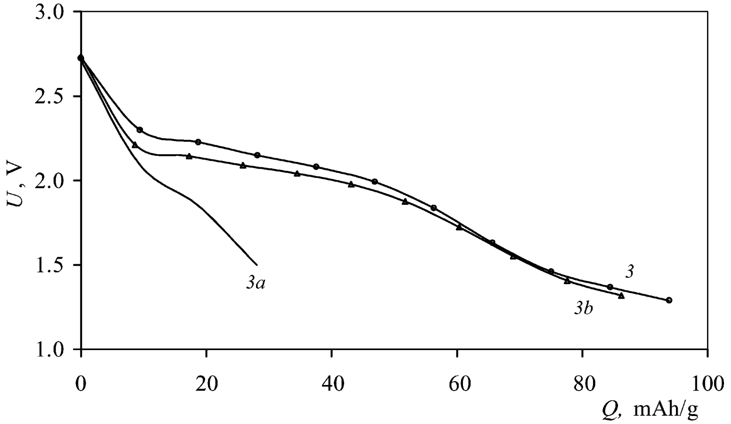


FIGURE 3 The first cycle chronopotentiometric discharge curves of the cathodes based on the polyenepolysulfide (experiment 3) and its fractions 3a and 3b (a model lithium cells).

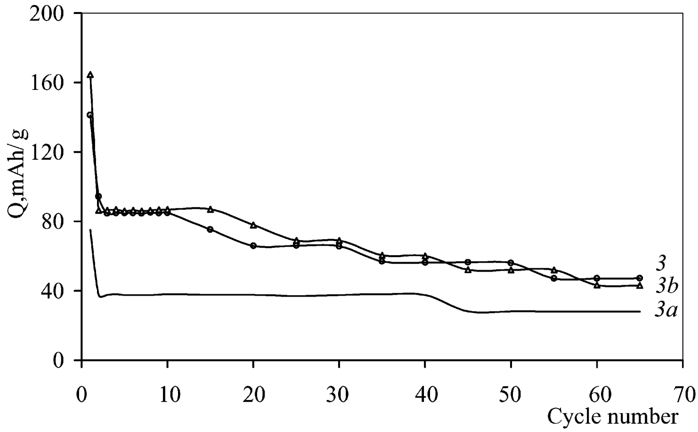


FIGURE 4 Discharge capacity (Q) vs. cycle number for cathodes based on the polyenepolysulfide (experiment 3) and its fractions 3a and 3b (a model lithium cell).

show two plateaus in the potential ranges of 2.30–2.20 and 2.10–1.90 V indicating that the process of electrochemical reduction of the polymers is multistage. The character and capacity of the discharge for a cathode based on the insoluble fraction (3a) significantly differ (Figure 3).

Prolonged cycling of the cathodes based on the net polymer (experiment 3) and its soluble (3b) and insoluble (3a) fractions in model lithium rechargeable cells, in potential range of 1.25–2.80 V, with the current density of 0.25 mA·cm^{-2}, shows a drastic drop of the capacity after the first cycle, stable cycling up to tenth, fifteenth and fortieth cycles, respectively, and an insignificant decrease of the capacity upon cycling up to sixty fifth cycles (Figure 4). Such behavior, characteristic of some polysulfide polymers[6,11] and elemental sulfur,[6–11,39] may be due to the formation of lithium mono- and disulfides which are, correspondingly, insoluble and poorly soluble in the electrolyte and thus are difficult to oxidize. These sulfides partly remain as suspensions and deposits, inactive in the subsequent redox processes, and partly precipitate on the surface of electrodes, thus preventing complete reduction and oxidation of the polymer. As a result, kinetics of the redox process worsens. Cathodes based on the net polymer (experiment 3) and its soluble fraction (3b) have similar values of the discharge capacity (142–56 and 167–52 mA·h·g^{-1}) over the whole cycling range (Figure 4).

As mentioned above, the fraction 3b possesses higher electroconductivity and sulfur content (59.1%) as compared to the net polymer (experiment 3) and its insoluble fraction (3a) and thus, seemingly, makes a major contribution to the electrochemical activity of the net polymer.

In conclusion, reaction of sodium acetylides with elemental sulfur in liquid ammonia affords polyenepolysulfides of complex composition, containing various polymeric blocks. These compounds possess paramagnetism, electrochemical activity and provide for the cycling of cathodes derived thereof in model lithium rechargeable cells.

EXPERIMENTAL

IR spectra were recorded on a Bruker IFS 25 instrument in pellets (KBr). ^{1}H NMR (400.13 MHz) were taken on a Bruker DPX-400 spectrometer in $CDCl_3$, HMDS as an internal standard.

ESR spectra were recorded at room temperature using a SE/X-2547 Radiopan (Poland) spectrometer equipped with a magnetometer and a high frequency gauge. Concentrations of paramagnetic centers were calculated by known techniques[40] using calibrated standards based on ultramarine and 2,2-diphenyl-1-picrylhydrazyl.

In electrochemical experiments, we used thin-layer two-electrode cells of disk type with lithium anode and aluminum cathodes (1.5 cm^2) covered with carbon and a composite of polymer, activated coal and polyethylene oxide in 65:30:5 wt% ratio. Porous polypropylene was used as a separator. The electrolyte used was 2 M solution of $(CF_3SO_2)_2NLi$ in a 1:1 mixture of 1,2-dimethoxyethane and 1,3-dioxolane. Cyclic voltammograms were taken at the potential scan rate of 1 $mV \cdot s^{-1}$ in potential range of 1.25–3.00 V on Potentiostate PI-50-1. Cycling of the cells was carried out on a bench testing unit for chemical power sources in potential range of 1.25–2.8 V using current density of 0.25 mA/cm^2.

Synthesis of Poly(ethynethiol) (Na:S, 1:1)

a. Ammonia (500 mL) was condensed into a 1-L four-necked flask (equipped with a mechanical stirrer, a bubbler, a thermometer and a condenser) cooled to −40°C (acetone/dry ice). To the flask, 0.1 g of $FeCl_3$ and 2.3 g (0.1 g-atom) of sodium in small pieces were added over 40 min upon stirring until complete disappearance of the blue color. Into the resultant suspension of sodium amide, acetylene was fed for 1 h upon vigorous stirring. Afterwards, under a stream of acetylene, fine-powdered sulfur (3.2 g, 0.1 g-atom) was added to the reaction mixture over 40 min. After addition of the last sulfur portion, the mixture was stirred for 3 h. Then, ~2/3 of the ammonia volume was removed.

To the resultant suspension of sodium ethynethiolate, 150 mL of 10% aqueous solution of NH_4Cl was slowly added by drops upon stirring. The mixture was allowed to stay for 12 h. The precipitate formed was filtered off, washed with H_2O (until negative reaction for chloride ions), acetone (10 mL) and ether (10 mL), and dried under vacuum for 6 h to give 2.8 g (48.3%) of a brown powder, m.p. 118–120°C, S 67.5% (experiment 1).

b. Ammonia (2000 mL) was condensed into a 3-L four-necked flask (equipped with a mechanical stirrer, a bubbler, a thermometer and a condenser) cooled to −40°C (acetone/dry ice). To the flask, 0.1 g of $FeCl_3$ and 23.0 g (1.0 g-atom) of sodium in small pieces were added over 1 h upon stirring until the blue color completely disappeared. To the resultant suspension of sodium amide, acetylene was fed for 8 h upon vigorous stirring. Afterward, under a stream of acetylene, fine-powdered sulfur (32.0 g, 1.0 g-atom) was added to the reaction mixture over 1 h. After addition of the last sulfur portion, the mixture was stirred for 3 h and allowed to stay overnight. Then, the mixture was treated with a saturated aqueous solution of NH_4Cl (55.0 g) in 200 mL of water. Further treatment (analogous to the experiment 1) gave 17.0 g (30.0%) of a brown powder, m.p. 96–98°C, S 55.3%.

Under conditions of experiment 1, 2.4 g (41.4%) of a dark-brown powder, m.p. 122–124°C, S 56.1% (experiment 3) were obtained.

Employment of the Na:S molar ratio of 1:2 (experiment 4), 1:3 (experiment 5), and 1:4 (experiment 6) under analogous conditions gave 2.3 g (50.0%, m.p. 118–120°C, S 84.1%), 4.2 g (79.0%, m.p. 120–122°C, S 87.9%), and 4.8 g (63.0%, m.p. 119–120°C, S 84.6%) of the product (a brown powder) respectively.

Fractionation of the Polymer from Experiment 3

The polymer obtained in experiment 3 (2.0 g) was extracted with benzene in a Soxhlet apparatus (5 h) to afford 1.12 g of a benzene-insoluble residue (m.p. 138–140°C, S 52.3%) (3a). From the benzene extract, 0.7 g of polymer 3b was obtained (m.p. 89–92°C, S 59.1%).

Methylation of a Sodium-Ethynylpolysulfides Mixture

Ammonia (100 mL) was condensed into a 200-mL four-necked flask (equipped with a mechanical stirrer, a bubbler, a thermometer and a condenser) placed into a vessel with cooling mixture (acetone and dry ice). To the flask, 0.1 g of $FeCl_3$ and 0.23 g (0.01 g-atom) of sodium in small pieces were added over 40 min, with the following stirring until complete disappearance of the blue color. To the resultant suspension of sodium amide, acetylene was passed for 1 h upon vigorous stirring. Afterwards, fine-powdered sulfur (0.32 g, 0.01 g-atom) was added to the reaction mixture over 40 min. After addition of the last sulfur portion, the mixture was stirred for 3 h and methyl iodide (4.26 g, 0.03 mmol) was added. The mixture was stirred for 2 h, the residue was extracted with $CDCl_3$, the extract was washed with H_2O (2 × 15 mL), dried over $MgSO_4$, and analyzed by ^1H NMR.

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