

Ethynedithiol-Based Polyeneoligosulfides as Active Cathode Materials for Lithium-Sulfur Batteries

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ABSTRACT: Ethynedithiol-based polyeneoligosulfides have been synthesized in 96% yield by the reaction of sodium acetylides (HC≡CNa, NaC≡CSNa) and elemental sulfur through the Na—C_{sp} bond in liquid ammonia with the following spontaneous polymerization of ethynedithiols (HSC≡CSH) formed by the hydrolysis. The polyeneoligosulfides synthesized are brown powders (up to 77% sulfur content, mp 128–184°C), partially soluble in organic solvents. They are high-resistance semiconductors (10⁻¹³ to

10⁻¹⁴ S cm⁻¹), possess paramagnetic (10¹⁷ to 10¹⁸ spin g⁻¹) and redox properties. The oligosulfides obtained, being redox systems capable of reversible redox processes, provide high values of discharge capacity (345–720 mA h g⁻¹) of rechargeable lithium-sulfur batteries. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 784–787, 2008

Key words: ethynedithiol; polyeneoligosulfides; lithium-sulfur batteries

INTRODUCTION

Over the last decade, research in the development of new lithium-sulfur rechargeable batteries has drawn attention to high sulfur content redox polymers as potential active components of cathode compositions.^{1–9} Among them, of a special interest, are electroconductive polymers, since, theoretically they should improve electrons transfer to the outer circuit.¹⁰

Recently,¹¹ searching for new approaches to electroconductive polymers with thiol, thione, and polysulfide structures, we have developed a method for the preparation of polyeneoligosulfides – derivatives of acetylenic monothiols (ethynethiols and ethynehydro-polysulfanes), based on the reaction of sodium monoacetylides with elemental sulfur in liquid ammonia.

In the present work, we briefly report on synthesis and properties of the ethynedithiol oligomers, a new group of polyeneoligosulfides, which are promising active cathode components of lithium-sulfur batteries.

EXPERIMENTAL

Methods

IR spectra of the products were run on a "Bruker IFS 25" instrument in KBr pellets.

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ESR spectra were recorded at room temperature using a SE/X-2547 Radiopan (Poland) spectrometer equipped with a magnetometer and a high frequency gauge.

In electrochemical experiments, we used thin-layer two-electrode cells of coin type with lithium anode and aluminum cathodes (1.5 cm²) 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 2M solution of (CF₃SO₂)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 s⁻¹ in potential range of 1.25–3.00 V on Potentiostat 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 the ethynedithiol oligomers

Oligosulfide I

To sodium acetylide, prepared from sodium (1.15 g, 0.05 g-atom) in liquid ammonia (500 mL), was added sulfur (1.60 g, 0.05 g-atom) for 40 min. The mixture was stirred for 2 h, and then another portion of sulfur (1.15 g, 0.05 g-atom) was added under stirring over 1 h. Afterwards, sulfur (1.60 g, 0.05 g-atom) was added for 40 min. The mixture was stirred for 3 h, then 2/3 of the ammonia volume was removed. The resultant mixture was poured into 100 mL of

TABLE I
Synthesis Conditions, Yields, and Characteristics
of Ethynedithiol-Based Polyeneoligosulfides

Sample	Na : S ratio (g-atom)	Yield (%)	mp (°C)	Found, S, (%)	Elementary unit
I	1 : 1	95.6	128–130	68.9	C ₄ S ₃
II	1 : 1	71.2	138–140	69.3	C ₂ H ₂ S ₂
III	1 : 1	44.9	178–180	64.7	C ₄ H ₄ S ₃
IV	1 : 2	61.6	170–171	63.4	56% C ₂ HS 44% C ₂ S ₂
V	1 : 3	49.7	173–174	76.0	77% C ₂ S ₂ 23% C ₂ S ₃
VI	1 : 4	33.3	182–184	77.0	69% C ₂ S ₂ 31% C ₂ S ₃

cooled 10% aqueous solution of NH₄Cl. The mixture was allowed to stay at room temperature for 12 h. The oligomer I formed was filtered off, washed with H₂O (until negative reaction for chloride ions), acetone and ether and dried in vacuum at room temperature for 6 h to give 4.30 g (95.6%) of oligosulfide I as brown powder (Table I).

Oligosulfide II

Synthesized analogously, except for additional hydrolysis of the reaction mixture, carried out after the ammonia removal by the addition of NH₄Cl (5.50 g) solution in water (150 mL). The brown powder obtained was refluxed in dry benzene (100 mL) with Dean-Stark trap for 2.5 h. The solid residue was filtered off and dried in vacuum (until the constant weight) to afford oligosulfide II (71.2%) as brown powder (Table I).

Oligosulfide III

Synthesized analogously, except for additional extraction with hot benzene in Soxhlet apparatus. The residue was dried in vacuum (until the constant weight) to give oligosulfide III (44.9%) as brown powder (Table I).

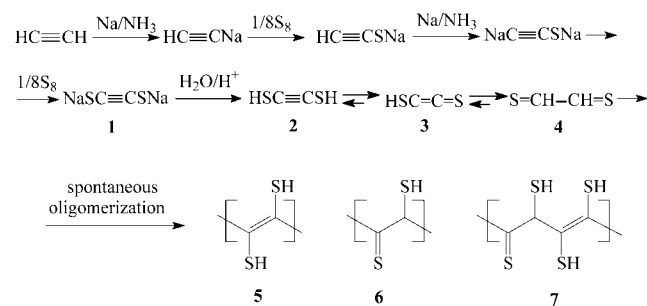
Oligosulfides IV–VI

Synthesized analogously, but the Na : S molar ratios were 1 : 2, 1 : 3, 1 : 4. After additional treatment with benzene (refluxing with Dean-Stark trap for 2.5 h, extraction in Soxhlet apparatus for 5 h), oligosulfides IV–VI (brown powders) were prepared, in 61.6%, 49.7%, 33.3% yields, respectively (Table I).

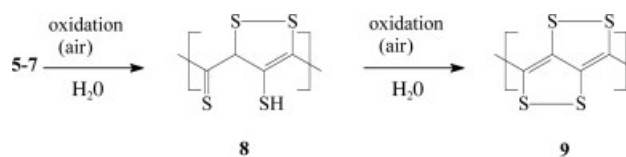
RESULTS AND DISCUSSION

The reaction of acetylene, elemental sulfur, and metallic sodium in liquid ammonia (according to the procedure described by Brandsma^{12–14}) gives sodium ethynedithiolate **1**. The latter undergoes hydrolysis to afford

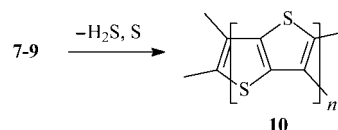
thiol **2**. Further spontaneous oligomerization of ethynedithiol **2** and its tautomers **3**, **4** leads to the formation of new polyeneoligosulfides containing the blocks **5–7**.



All stages of the reaction, beginning from the dithiolate **2** synthesis and ending up with the compounds **2–4** oligomerization, are carried out in one pot. Yield of the oligomers, being depended on the synthesis conditions, methods of the reaction mixtures treatment, purification of the products obtained, reaches, in the best case, 96% (calculated per elemental unit). Along with the structural fragments **5–7** the real structures of oligomers prepared include products of their further transformations – dithiolene blocks **8**, **9** formed due to oxidation of thiol moieties in air:



Treatment of the oligomers with hot benzene is likely to involve the formation of oligothienothiophene structure **10** (due to desulfurization of the **7–9** blocks):



The oligomers synthesized are brown powders (sulfur content 63–77%, mp 128–184°C) partially

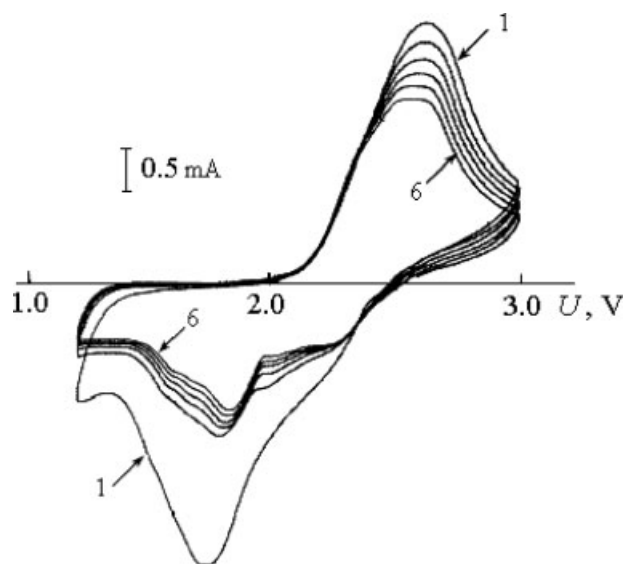


Figure 1 Typical cyclic voltammograms of ethylenedithiol-based polyeneoligosulfides for first to sixth cycles (vs. Li/Li^+).

soluble in organic solvents (ether, benzene, chloroform, acetone).

In the IR spectra of the oligomers synthesized, there is a broad weakly resolved band with maxima at $1476\text{--}1453$, $1435\text{--}1432$, $1413\text{--}1408$, and $1367\text{--}1325\text{ cm}^{-1}$, which corresponds to the vibrations of polyeneoligothiol and polyeneoligosulfide blocks 7–9 as well as skeleton of oligothienothiophene structures 10.^{15–20} Maxima in the regions of $1290\text{--}1280$, $1250\text{--}1221$, $1200\text{--}1149\text{ cm}^{-1}$ are assigned to the C–S moiety in structures 6–8.^{20–23} According to^{23–26} the weak indistinct maxima at $856\text{--}802$, $790\text{--}730$, $691\text{--}606$, $592\text{--}547\text{ cm}^{-1}$ are likely to belong to the stretching vibrations of the C–S bonds in various oligomer structural units. IR spectra of the oligomers I–VI in the region of $485\text{--}412\text{ cm}^{-1}$ show two absorption bands with maxima at $425\text{--}430$ and $466\text{--}473\text{ cm}^{-1}$ corresponding to stretching vibrations of the S–S bonds that is indicative of the presence of electrochemically active fragments 8 and 9 in the structure of all polyeneoligosulfides synthesized.^{21,23–25} Depending on the preparation route intensity of these bands varies that is explained by the change of a number of these fragments in the molecules of the oligomers as compared with the blocks 5–7, and 10 containing no S–S bonds. So in the oligomer III, the stretching vibrations of the S–S bonds appear as two bands of the same intensity with the absorptions maxima at $425\text{--}470\text{ cm}^{-1}$. For the oligomers IV, II, I, V, and VI intensity of high-frequency band with maximum at $466\text{--}473\text{ cm}^{-1}$ gradually increases that points to the larger numbers of blocks containing electrochemically active S–S bonds.

The ESR and electroconductivity data are in keeping with structure and properties of the oligomers

obtained. Polyeneoligosulfides I–IV possess electroconductivity of the order of $10^{-14}\text{ S cm}^{-1}$ and polyeneoligosulfides V, VI – $10^{-13}\text{ S cm}^{-1}$. They also show paramagnetism (10^{17} to $10^{18}\text{ spin g}^{-1}$). The EPR spectra contain two different (in shape, width, and g -factor) anisotropic signals that are indicative of inhomogeneous composition of the oligomers synthesized. Asymmetric singlet in the region of g -factor for free radicals (from 2.0043 to 2.0072) corresponds to the presence of polyconjugated blocks 5, 9, 10 in the structure of the oligomers I–VI. Paramagnetic and semiconducting properties of these blocks are determined by polaron nature.²⁷ According to the characteristics and g -factor value (2.0280) the second broad signal can be assigned to trisulfide S_3^- anion-radicals.^{28,29} Formation of such radicals in the process of oligomers preparation confirms the presence of the blocks 8,9 bearing electrochemically active S–S bonds in the polyeneoligosulfides I–VI.

Shapes of cyclic voltammograms of all the oligosulfides synthesized are similar (Fig. 1). It confirms the presence of di- and polysulfides blocks (like 8 and 9) in their macromolecules. Cathode polarization involves typical step-by-step reduction of the polysulfide moieties at 2.5 and 1.8 V with respect to Li/Li^+ . Subsequent oxidation of lower lithium sulfides formed proceeds at 2.4–2.5 V.

Redox activity of oligosulfides-based cathodes of lithium cells has been studied in galvanostatic mode. The changes in specific discharge capacity of the cathodes during cycling are given in Figure 2. The values of discharge capacity of samples prepared using an equimolar Na : S ratio (oligosulfides I, II, III) correlate with sulfur content (Fig. 2). Oligosulfide IV obtained using an atomic ratio of Na : S = 1 : 2 contains less amount of sulfur (63.4%, Table I) than oligosulfide III, but cathodes with its show higher values of discharge capacity (Fig. 2). It indicates that in the sample IV sulfur is presented mainly in polysulfide forms of the fragments 8 and 9, whereas in

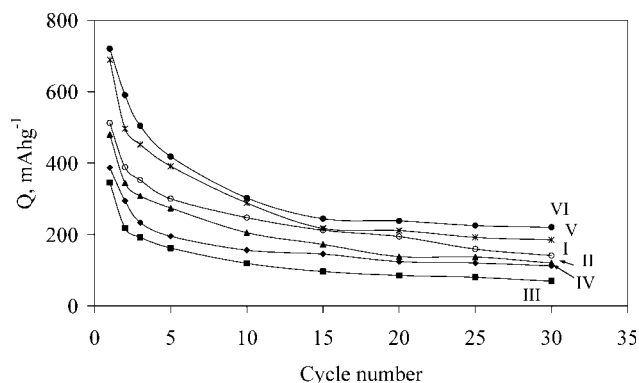


Figure 2 Specific discharge capacity (Q) vs. cycle number for cathodes based on the polyeneoligosulfides I–VI (a model lithium cell).

oligosulfide III prevail oligothienothiophene blocks 10. The increase of sulfur content in oligosulfides prepared with the atomic ratio of Na : S = 1 : 3 and 1 : 4 (oligosulfides V, VI) is accompanied by the growth of discharge capacity up to 720 mA h g⁻¹ (1st cycle) and to 212 mA h g⁻¹ (30th cycle). This is another evidence for the predomination of polyeneoligosulfide blocks 8 and 9 in macromolecules of these oligomers, which show higher values of electroconductivity.

The drastic drop of the capacity on the first cycles is caused by its irreversible loss because of partial removal of active polysulfide sulfur from the cathode surface that is a common problem for lithium-sulfur batteries. The character of the capacity – cycle number dependence (Fig. 2) demonstrates that all the oligomers synthesized provide stable prolonged cycling of cathode and are promising as active cathode components for rechargeable lithium-sulfur batteries of new generation.

CONCLUSIONS

In conclusion, the oligomers of ethyenedithiols, polyeneoligosulfides, synthesized from acetylene and elemental sulfur in a one port procedure, possess conductivity, paramagnetic, and redox properties; they are also promising materials for the design of cathode compositions of lithium-sulfur rechargeable batteries.

References

- Novak, P.; Muller, K.; Santhanam, K. S. V.; Haas, O. *Chem Rev* 1997, 97, 207.
- Scrosati, B. *Application of Electroactive Polymers*; Chapman & Hall: London, 1993.
- Roncali, J. *Chem Rev* 1992, 92, 711.
- Fanghänel, E.; Richter, A. M.; Kordts, B.; Beye, N. *Phosphorus, Sulfur, Silicon Relat Elem* 1989, 43, 165.
- Trofimov, B. A. *Sulfur Rep* 2003, 24, 283.
- Trofimov, B. A.; Vasil'tsov, A. M.; Petrova, O. V.; Mikhaleva, A. I.; Myachina, G. F.; Korzhova, S. A.; Skotheim, T. A.; Mikhaylik, Yu. V.; Vakul'skaya, T. I. *Izv AN Ser Khim* 2002, 9, 1569 [*Russ Chem Bull Int Ed* 2002, 51, 1709].
- Trofimov, B. A.; Parshina, L. N.; Gusarova, N. K.; Ivanova, N. I.; Myachina, G. F.; Kovalev, I. P.; Skotheim, T. A. *Sulfur Lett* 2002, 25, 219.
- Skotheim, T. A.; Trofimov, B. A.; Mal'kina, A. G.; Kovalev, I. P. *US Patent* 5,529,860 (1997).
- Skotheim, T. A.; Trofimov, B. A.; Mal'kina, A. G. *US Patent* 6,174,621 (1996).
- Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*; Marcel-Decker: New York, 1998.
- Trofimov, B. A.; Mal'kina, A. G.; Dorofeev, I. A.; Myachina, G. F.; Rodionova, I. V.; Vakul'skaya, T. I.; Sinegovskaya, L. M.; Skotheim, T. A. *Phosphorus, Sulfur, Silicon Relat Elem* 2004, 179, 35.
- Brandsma, L.; Wijers, H. E.; Arens, J. F. *Recl Trav Chim Pays-Bas* 1962, 81, 583.
- Brandsma, L.; Wijers, H. E.; Jokers, C. *Recl Trav Chim Pays-Bas* 1964, 83, 208.
- Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier: Amsterdam-Oxford-New York-Tokyo, 1988.
- Trofimov, B. A.; Skotheim, T. A.; Andriyankova, L. V.; Mal'kina, A. G.; Myachina, G. F.; Korzhova, S. A.; Vakul'skaya, T. I.; Kovalev, I. P.; Mikhaylik, Yu. V. *Izv AN Ser Khim* 1999, 462 [*Russ Chem Bull Int Ed* 1999, 48, 459 (Engl. Transl.)].
- Trofimov, B. A.; Skotheim, T. A.; Mal'kina, A. G.; Sokolyanskaya, L. V.; Myachina, G. F.; Korzhova, S. A.; Stoyanov, E. S.; Kovalev, I. P. *Izv AN Ser Khim* 2000, 865 [*Russ Chem Bull Int Ed* 2000, 49, 863 (Engl. Transl.)].
- Trofimov, B. A.; Skotheim, T. A.; Mal'kina, A. G.; Sokolyanskaya, L. V.; Myachina, G. F.; Korzhova, S. A.; Vakul'skaya, T. I.; Klyba, L. V.; Stoyanov, E. S.; Kovalev, I. P.; Mikhaylik, Yu. V. *Izv AN Ser Khim* 2001, 245 [*Russ Chem Bull Int Ed* 2001, 50, 253 (Engl. Transl.)].
- Trofimov, B. A.; Mal'kina, A. G.; Sokolyanskaya, L. V.; Nosyryeva, V. V.; Myachina, G. F.; Korzhova, S. A.; Vakul'skaya, T. I.; Klyba, L. V.; Stoyanov, E. S.; Skotheim, T. A.; Mikhaylik, Yu. V. *Izv AN Ser Khim* 2002, 276 [*Russ Chem Bull Int Ed* 2002, 51, 282 (Engl. Transl.)].
- Jensen, K. A.; Henriksen, L. *Acta Chem Scand* 1968, 22, 1107.
- Petukhova, N. P.; Dontscova, N. E.; Prilezhaeva, E. N. *Izv AN SSSR Ser Khim* 1984, 194.
- Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Methuen and Co. LTD: London, 1963.
- Spinner, E. J. *Org Chem* 1958, 23, 2037.
- Lozach, N. *Record Chem Progr* 1959, 20, 23.
- Kazitsina, L. A.; Kupletskaya, N. B. *Application of UV, IR and NMR Spectroscopy in Organic Chemistry*; Vyshaya shkola: Moscow, 1971 (in Russian).
- Nakanisi, K. *Infrared spectra and structure of organic compounds*; Mir: Moscow, 1965 (in Russian). [*Infrared Absorption Spectroscopy*; Holden-Day, Inc.: San Francisco, 1962].
- Trofimov, B. A.; Amosova, S. V. *Divinylsulfide and its derivatives*; Nauka: Novosibirsk, 1983.
- Hauze, E.; Nechtschein, M. *Phys Rev B* 1996, 53, 14309.
- Lunsford, J. H.; Johnson, D. P. *J Chem Phys* 1973, 58, 2079.
- Gobeltz, N.; Demortier, A.; LeliEur, J.-P.; Simon, P.; Duhayon, C. *New J Chem* 1997, 21, 423.