Vinyl Ethers with Polysulfide and Hydroxyl Functions and Polymers Therefrom as Binders for Lithium–Sulfur Batteries

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ABSTRACT: Bis-[3-(vinyloxyethoxy)-2-hydroxypropyl-]polysulfides (BVPS) have been prepared by reacting ethylene glycol vinyl glycidyl ether (EGVGE) with Na_2S_4 in the presence of $NaHCO_3$ and a phase transfer catalyst, triethylbenzylammonium chloride. The polysulfides obtained are inactive in radical polymerization but polymerize readily upon thermal initiation (140°C, 1 h) or in the presence of cationic catalysts [$BF_3 \cdot OEt_2$, CF_3COOH, $H(AuCl_4) \cdot 4H_2O$, $LiBF_4$-dimethoxyethane, 20–70°C]. Polymerization leads to the formation of crosslinked polymers. It has been shown that BVPS and their polymers can be used as active binders in cathode compositions of lithium–sulfur power sources. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4051–4055, 2006

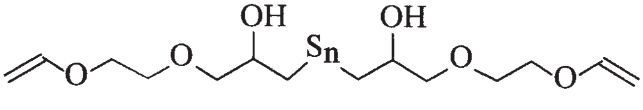
Key words: vinyl ethers; cationic polymerization; polysulfides; binders

INTRODUCTION

Lithium–sulfur rechargeable batteries, in which sulfur is the main component of the cathode material, can theoretically possess significantly higher specific energy as compared to lithium-ion accumulators,[1] so that is why in spite of a number of problems encountered, investigations in this field are being continued.[2–5]

An important part of a sulfur cathode is the binder, which ensures permanent contact between sulfur, conducting component (coal, graphite, or their mixture), and current collector. Common binders are represented by various electrochemically inactive polymers (most often, polyethylene oxide,[6,7] which lower the specific capacity of the cathode. In principle, the use of polysulfide polymeric networks as cathode binder elements may considerably improve electrochemical characteristics of lithium–sulfur battery.

In the present work, polyfunctional divinyl ethers with polysulfide and hydroxyl functions, bis[3-(vinyloxyethoxy)-2-hydroxypropyl]polysulfides (BVPS), have been studied as binder components of sulfur cathode, capable of *in situ* formation of polymeric polysulfide matrix.



n = 2, 3

This work is concerned with the synthesis of BVPS with various length of the polysulfide chain (n = 2, 3) and a study of their polymerization and suitability for using in cathode compositions of lithium–sulfur batteries.

EXPERIMENTAL

Materials

Chemically pure sodium sulfide $Na_2S \cdot 9H_2O$ and elemental sulfur were used. The purity of ethylene glycol vinyl glycidyl ether (EGVGE) was 99.99% (GLC control). Physical constants of EGVGE corresponded to the literature (bp 77°C/6 mm Hg, n_D^{20} 1.4480, d_4^{20} 1.0333.[8]

Methods

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

GLC control was performed on a LXM-80 chromatograph, column: 3000 × 3 mm^2; liquid phase: 1% PEG 20,000; solid phase: NaCl; detector: catarometer; and gas carrier: helium.

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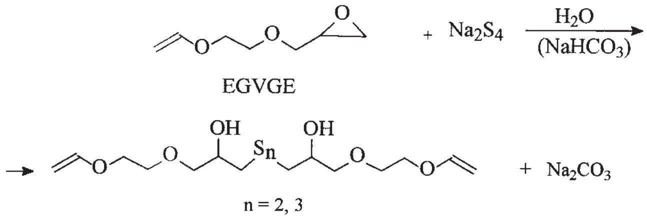
TABLE I
Effect of Reaction Conditions on the Yield and Composition of BVPS

Run	Temperature (°C)	Yield (%)	Found (%) C	H	S	n^a
1[b]	60	96.1	45.54	7.12	20.00	2.3
2[b]	20	87.6	43.50	6.78	24.89	2.9
3	20	77.6	42.91	7.94	24.52	3.0
4	30	69.1	43.91	6.91	24.23	2.9
5	60	48.8	43.13	8.14	26.63	3.3

[a] Number of sulfur atoms in the polysulfide (according to elemental analysis).
[b] Na_2S_4 was added to EGVGE.

^{1}H-NMR spectra were recorded on a Bruker Avance DPX 250 spectrometer (250 MHz) in $CDCl_3$ and referenced to internal HMDS.

The synthesis of BVPS from EGVGE was carried out as follows:



The method used differs from the known one[9] in that (a) an additional reactant, sodium hydroxycarbonate, is used for trapping alkali formed, (b) the reaction is carried out in the presence of a phase-transfer catalyst, triethylbenzylammonium chloride (TEBA), and (c) the product is isolated by the extraction with diethyl ether after dilution of the reaction mixture with water. Such a substantial modification of the method[9] turned out to be necessary for the preparation of BVPS acceptable for polymerization and containing no alkaline decomposition products of polysulfides formed (corresponding thiols) and products of alkaline hydrolysis of the starting EGVGE (namely, glycerol vinyloxyethyl ether).

Synthesis of BVPS (typical procedure)

Sodium tetrasulfide, prepared from 57.6 g (0.68 mol) of $Na_2S·9H_2O$ and 21.9 g (0.67 mol) of elemental sulfur upon heating and stirring (60°C, 1.5 h) (the product represents a uniform dark-red liquid), was added dropwise to a stirred mixture of 5.7 g of TEBA, 57.1 g (0.68 mol) of $NaHCO_3$, and 82.3 g (0.57 mol) of EGVGE over 3 h, while keeping the required temperature (Table I). After 24 h, the reaction mixture was diluted with 200 mL of cold water and extracted with diethyl ether (6 × 50 mL). The ether extracts were washed with water until neutral reaction and dried over K_2CO_3. Ether was removed, and the residue was kept under vacuum until constant weight (2 mmHg, room temperature) to give 92.5 g of BVPS ($n = 3$) (87.6% yield), a dark-colored liquid soluble in most organic solvents (Table I, run 5). Found, %: C 43.62; H 6.99; S 24.10. $C_{14}H_{26}O_6S_3$. Calcd., %: C 43.50; H 6.78; S 24.89.

Typical example of polymerization

To 1.00 g of BVPS, 0.001 g of the 10% solution of BF_3OEt_2 in acetonitrile was added under argon; the mixture was stirred and heated at 70°C for 3 h. The polymer obtained (unsoluble yellow transparent solid block) was ground, washed off with methanol, dried under vacuum till constant weight, and analyzed.

Analogous procedures were employed for the polymerization with other cationic catalysts—CF_3COOH (10% solution in acetonitrile), $H(AuCl_4)·4H_2O$ (0.5% solution in acetonitrile), complex $LiBF_4$-dimethoxyethane (10% solution of LiF_4 in dimethoxyethane, Table II).

In electrochemical studies, button cells with a lithium anode and an aluminum cathode coated with carbon and a composition of sulfur, activated carbon and BVPS in a ratio of 50:35:15 or 60:35:5 (mass %) were used. A 0.75*M* solution of $(CF_3SO_2)_2NLi$ in a 1:1 mixture of 1,2-dimethoxyethane and 1,3-dioxolane

TABLE II
Conditions of Polymerization of Bis-[3-(vinyloxyethoxy)-2-hydroxypropyl]polysulfides

Catalyst (wt %)	Temperature (°C)	Time (h)	Product consistence
AIBN, 2.00	60	40	Liquid
BP, 2.00	80	50	Liquid
DPC[a], 2.00	70	50	Liquid
None[b]	20	1	Liquid
None	140	1	Insoluble solid
S[c]	130	1	Insoluble solid
$BF_3 \cdot Oet_2$, 0.01	20	50	Elastic insoluble product
$BF_3 \cdot Oet_2$, 0.01	70	3	Insoluble solid
$H(AuCl_4)$ $4H_20$, 0.50	20[d]	~1 min	Elastic insoluble product
$H(AuCl_4)$ $4H_20$, 0.02	70	6	Elastic insoluble product
CF_3COOH, 0.1	20	~1 min	Elastic insoluble product
CF_3COOH, 0.01	20	30 min	Elastic insoluble product
$LiBF_4 \cdot$ DME, 1.00[e]	20	20	Insoluble solid
$LiBF_4 \cdot$ DME, 1.00[e]	50	6 min	Insoluble solid
$LiBF_4 \cdot$ DME, 0.50[e]	50	2	Insoluble solid
$LiBF_4 \cdot$ DME, 0.25[e]	70	24 min	Insoluble solid
$LiBF_4 \cdot$ DME, 0.10[e]	70	10 min	Insoluble solid
$LiBF_4 \cdot$ DME, 0.05[e]	70	15 min	Insoluble solid
$LiBF_4 \cdot$ DME, 0.01[e]	70	2	Insoluble solid

[a] Diacetyl peroxydicarbonate.
[b] UV irradiation.
[c] 60 wt %.
[d] Exothermic effect (up to 110°C).
[e] Complex with 1,2-dimethoxyethane.[12]

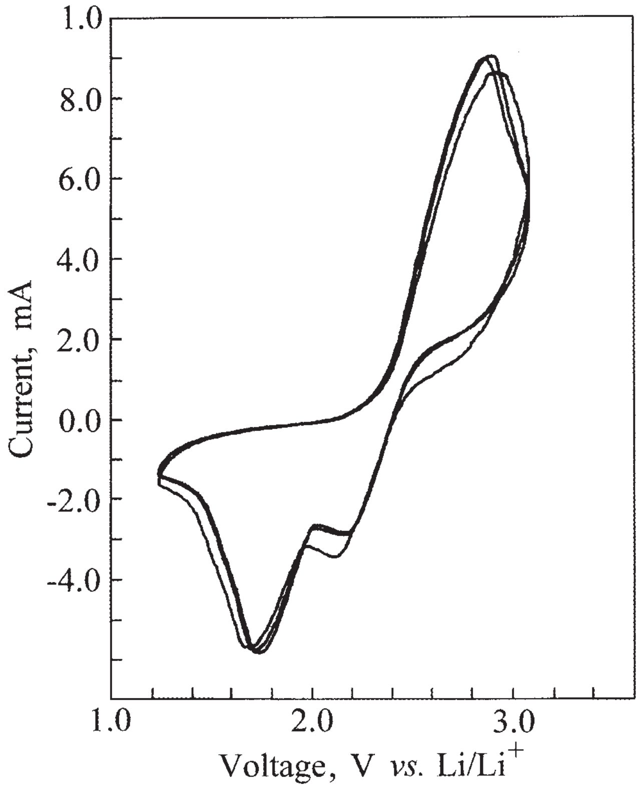


Figure 1 Cyclic voltammograms of the sulfur cathode with BVPS as binder in 0.75*M* $(CF_3SO_2)_2NLi$/DME:DO (1:1). Scan rate is 1 mV s^{-1}.

was employed as an electrolyte. Cyclic voltammograms were recorded using PI-50 potentiostat/galvanostat with an *X–Y* recorder in the 1.25–3.0 V potential range at a potential scan rate of 1 mV/s. Cell cycling was performed on a battery tester at a current density of 0.25 mA cm^{-2} in a voltage range from 1.25 to 2.80 V.

RESULTS AND DISCUSSION

A study of effect of reaction conditions on the yield and composition of BVPS has shown that the reaction can be directed to the formation of either di- or trisulfide by varying reaction temperature and reactant mixing order (Table I).

When EGVGE is added to a reaction mixture containing sodium tetrasulfide, a self-heating to 60°C is observed, and the yield of BVPS is 48.8%, while the sulfur content is 26.6%, corresponding to trisulfide (Table I, run 5).

BVPS, containing mainly disulfide ($n = 2.3$, sulfur content 20%), was obtained in 96.1% yield at the same temperature (self-heating) by introduction of sodium tetrasulfide into a reaction mixture with EGVGE (Table I, run 1).

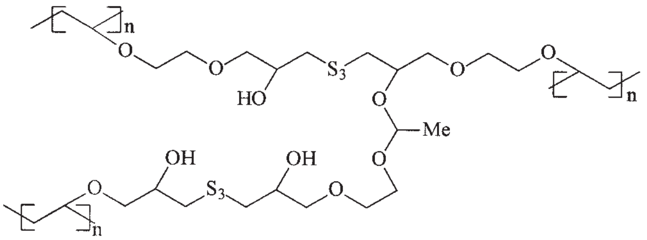
Under thermostating conditions (20 and 30°C), trisulfides are always formed (Table I, runs 2–4).

Structures of BVPS synthesized were confirmed by IR and NMR spectroscopy. In a well-resolved IR spectrum of BPVS, there is an intense band of stretching vibrations of hydroxyl groups (3439 cm^{-1}) and strong absorption bands at 2923 and 2875 cm^{-1} (C—H, —CH_2—), whereas vinyloxy groups show up at 822, 975, 1200, 1320, 1620, 1640, 3080, and 3115 cm^{-1}.[8] An intense absorption in the 1130–1037 cm^{-1} region is caused by stretching vibrations of ether groups. Weak bands at 737, 702, 610, 546, and 475 cm^{-1} are assigned to C—S and S—S stretchings, respectively.[10,11]

Characteristic frequencies of epoxy ring (840, 915, 3060 cm^{-1}), which are present in the spectrum of the starting EGVGE, are absent in the IR spectrum of BVPS.

^1H-NMR spectra of BVPS show peaks at 6.47 ppm (—CHO), 4.25, 4.08, 3.97 ppm (═CH—), 3.80, 3.63 ppm (OCH_2) and 3.07 ppm (OH), as well as peaks of CH_2S groups' protons at 2.89 ppm.

It has been found (Table II) that BVPS is inactive in the radical polymerization initiated by AIBN, dicetyl peroxydicarbonate (DPC), benzoyl peroxide (BP) (2%, 60, 70, and 80°C, 40–50 h) or UV irradiation, but readily polymerizes in the presence of 0.01–1% of cationic catalysts, $BF_3{\cdot}OEt_2$, $H(AuCl_4){\cdot}4H_2O$ (Table II).



BVPS polymerizes very effectively under the action of a latent catalytic system, $LiBF_4$—1,2-dimethoxyethane (Table II), developed by us earlier.[12] This system ensures controllable polymerization of BVPS in a wide temperature interval with acceleration above 50°C (reaction time at room temperature is 20 h).

According to IR spectroscopy, the cationic polymerization process is accompanied by polyaddition of hydroxyl groups to vinyloxy moieties, which results in extra crosslinking of the polysulfide network.

IR spectra of crosslinked polymers obtained show an intense absorption in the hydroxyl group stretching vibrations region at 3450 cm^{-1}. Acetal groups appear as a broad band at 1050–1080 cm^{-1}. The bands at 610, 550 cm^{-1}, and 470–450 cm^{-1} are assigned to C—S and S—S bonds.[10,11] A weak absorption in the C═C bond region (1620, 1320–1200, 960, and 820 cm^{-1}) is caused by the presence of terminal vinyloxy groups.

A study of BVPS interaction with elemental sulfur and sodium sulfide has shown that even on heating (120°C, 1.5 h), no sulfur insertion into BVPS molecules

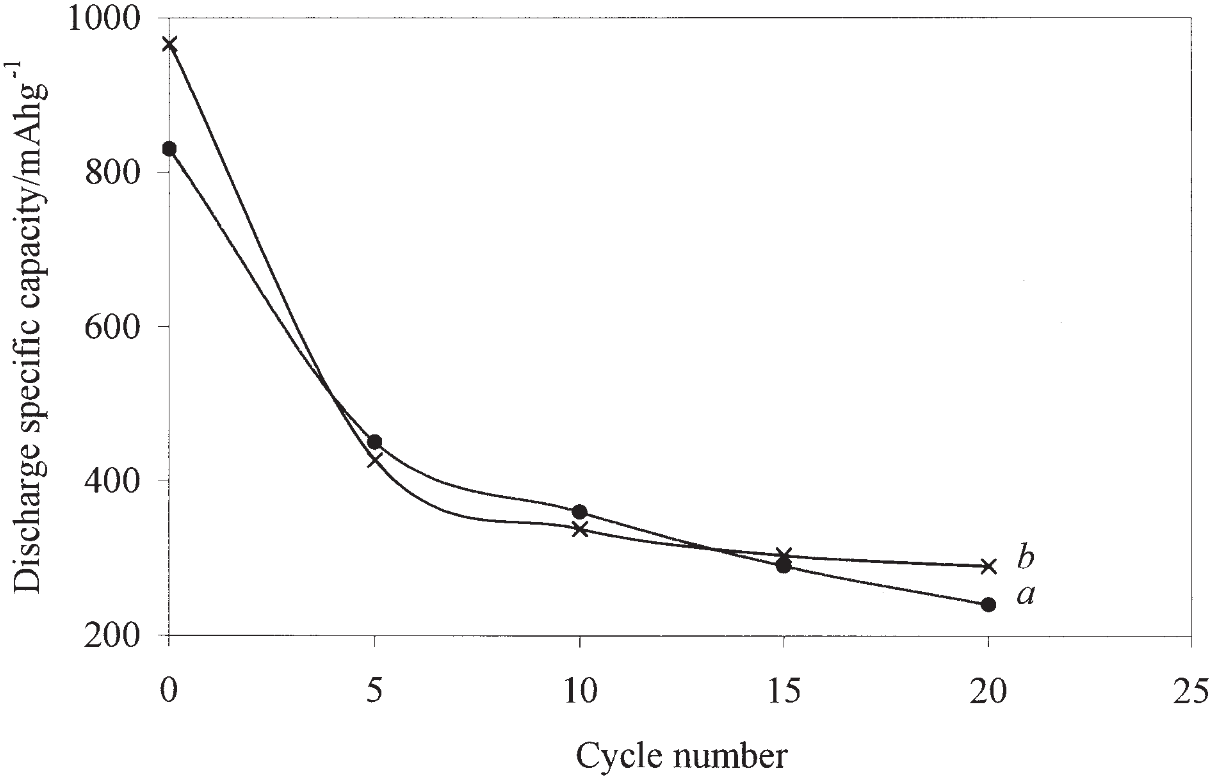
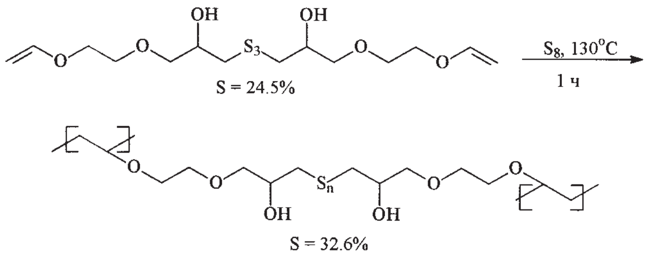


Figure 2 Specific discharge capacity (*Q*) versus cycle number for button cells with different electrolyte composition formulation: sulfur:carbon:BVPS = 50:35:15 (a) and 60:35:5 (b). Current density 0.25 mA/cm^2, potential cutoff 1.25 V.

occurs. Instead, a solution (up to 35% of sulfur) is formed, which is stable upon storage, and from which sulfur can be recovered by adding methanol.

Increasing the reaction temperature to 130°C (1 h) in the presence of 20–60 wt % of elemental sulfur leads to the formation of a structurized polymer, which represents a uniform solid transparent yellow material. The sulfur content in the crosslinked polymers obtained (after extraction of elemental sulfur with benzene in a Soxhlet apparatus) is up to 32.6% (n = 4), which corresponds to the covalent binding of sulfur by polysulfide moieties.

According to IR data, the polymerization proceeds at vinyl groups. The bands in the 3080, 3110, 1320, 1200, and 820 cm^{-1} region disappear, and the intensity of the C=C group's band at 1640 and 1620 cm^{-1} sharply decreases. An intense band of stretching vibrations of hydroxyl groups (3439 cm^{-1}) does not change.



Monomeric BVPS with an elongated polysulfide block was prepared by reacting BVPS with elemental sulfur in the presence of the system $Na_2S{\cdot}9H_2O$/TEBA/DMSO, which is well-known owing to its high activity in sulfur insertion reactions with S—S bonds of polysulfides.[13] BVPS obtained (20 and 45°C, 1 h, brown transparent oils) contain 4.4–7.5% more sulfur as compared to the starting BVPS. In contrast to sulfur solutions in BVPS, which lose elemental sulfur upon addition of ethanol, they are well-soluble in organic solvents. On long storing (2 years, 20°C), BVPS with an elongated polysulfide block polymerize to form a transparent uniform solid polymer.

Electrochemical testing of BVPS as a binder component of cathode composition for lithium–sulfur accumulators was performed using cyclic voltammetry and chronopotentiometry. It has been found that introduction of 5–15% of BVPS into a sulfur–carbon composition allows one to prepare cathode material, possessing good adhesion to the aluminum electrode core (solidification temperature 60–100°C). Cyclic voltammograms of a BVPS-based sulfur cathode show characteristic electrochemical reduction at potentials of 2.18 and 1.74 V and oxidation at 2.86 V (Fig. 1). Cycling of cathodes in button cell lithium batteries shows high values of the discharge capacity (830–960 mAh/g) at the first cycle (Fig. 2). Further cycling (up to the 5th cycle) is accompanied by a sharp capacity decrease, which is typical of sulfur cathodes and occurs due to partial irreversible loss of active sulfur from the cathode surface in a form of insoluble sulfur reduction products: lithium sulfides and disulfides. After the 5th cycle, the cycling stabilizes at a discharge capacity value of 450–240 mAh/g. The strong adhesion of the cathode composition to the electrode material is retained even with a 5% content of the BVPS binder in the composition. This gives opportunity to increase the content of electrochemically active sulfur in the cathode composition up to 60%. As a result, 16 and 21% discharge capacity increase at the 1st and 20th cycles, respectively, has been obtained [Fig. 2(b)].

CONCLUSIONS

Therefore, a new method for the synthesis of divinyloxyhydroxypolysulfides has been developed. These compounds have been shown to possess high activity in cationic and thermal polymerization and can be used as active binders in cathode compositions of lithium–sulfur power sources.

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