

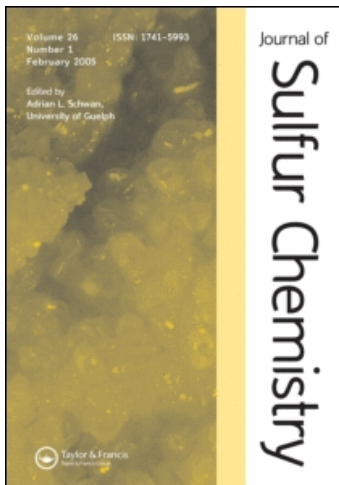
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Sulfurization of Polymers: A Novel Access to Electroactive and Conducting Materials

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SULFURIZATION OF POLYMERS: A NOVEL ACCESS TO ELECTROACTIVE AND CONDUCTING MATERIALS

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The article is a concise analysis of the author's group's systematic exploration of the scope and potential of a new general approach to the synthesis of sulfur-rich polyconjugated polymers by direct dehydrogenative sulfurization of common polymers (polyethylene, polyacetylene, polystyrene, polyvinylpyridine, polydiethylsiloxane) with elemental sulfur. The deeply sulfurized polymers thus formed, consist of functionalized redox-active polyene, polysulfide and polycondensed thiophene entities and related blocks, the ratio of which depends on the reaction conditions and starting polymer structure. This paves the simplest way to electroactive and conducting materials with tailor-made properties, which may find application (among others) as principal cathode components of advanced electrochemical energy storage devices, e.g. lithium rechargeable batteries.

Keywords: Sulfurization; Sulfurized polymers; Electroactive conducting materials; Cathode materials; Electrochemical energy storage devices

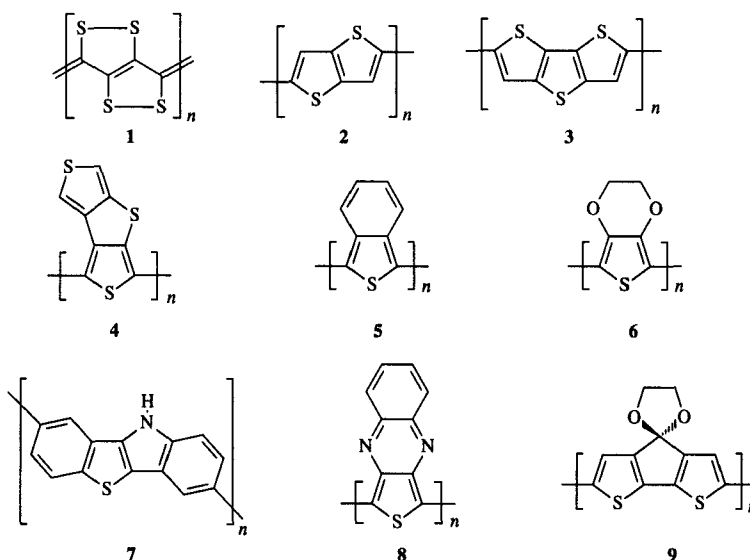
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1. INTRODUCTION

Over the last decade, sulfur-containing polymers with conjugated double bonds and heterocycles such as polythiophenes [1–4] and, particularly, polycondensed heterocyclic systems with dithiole or thiophene entities, such as poly(dithiolodithiole-3,6-diylidene) **1** [5], poly(thienothiophene) **2** [6–8], poly(dithienothiophenes) **3**, **4** [9–13], poly(isobenzo[*c*]thiophene) **5** [14,15], poly(3,4-ethylene-dioxythiophene) **6** [16], poly(benzothienoindole) **7** [17,18], polythieno[3,4-*b*]quinoxaline **8** [19], poly(4,4-ethylene-dioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene) **9** [20] (Scheme 1) and so forth, have attracted much interest and attention as synthetic metals and prospective materials for advanced electrochemical energy storage devices (rechargeable batteries) [2].

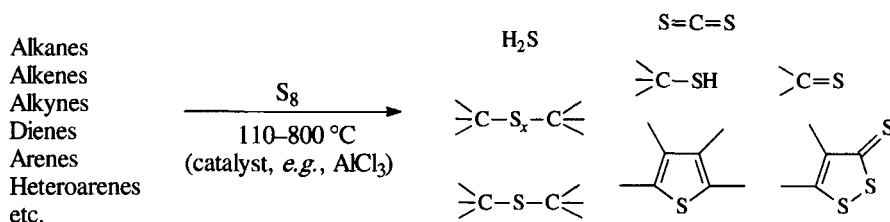


SCHEME 1

The introduction into such molecules of sulfur-centered reversible redox-active functions, such as thiol, thione, disulfide or polysulfide moieties, should improve substantially their properties as active cathode materials for secondary batteries with lithium or sodium anodes. However, to our knowledge, before this work, no data on condensed heterocyclic polymers, containing at least one thiophene ring and the above electroactive sulfur functions in their monomeric unit, have been published.

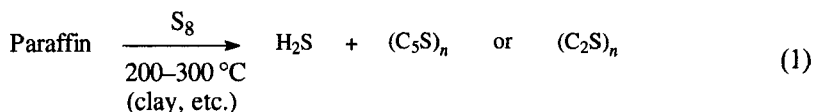
Recently, we have initiated a systematic study of the direct sulfurization (with elemental sulfur) of conventional polymers in the framework of a general concept that such an approach might be the most straightforward route to electroactive and conducting sulfur-rich polycondensed polymers with the thiophene moiety in their repeating units of the tailor-made structure.

The concept has stemmed from the common knowledge that elemental sulfur on heating with or without a catalyst is readily inserted into the C–H bond of diverse organic compounds to form further, depending on the reaction conditions, polysulfides, thiols, thiones, sulfides, thiophenes and dithiolothiones as well as alkenes, arenes, asphaltenes, etc., apart from usual hydrogen sulfide and carbon disulfide (Scheme 2) [21].



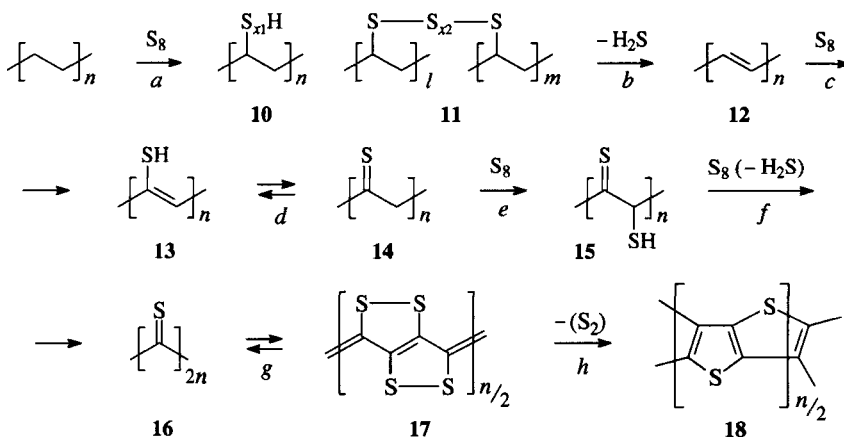
SCHEME 2

The final products of the paraffin sulfurization, as reported in old papers (for references see Ref. [21]) had compositions ranging from C_5S to C_2S but were not studied more closely:



A few papers on polyethylene cross-linking by elemental sulfur are known [22–24]. The chemistry of rubber vulcanization up to the manufacture of ebonite-like materials is well documented and continues to be developed. However, all these have little to do with the functionalized polycondensed polythiophenes we looked forward to synthesizing through the direct sulfurization of available polymers while developing the above concept.

The major expected reactions which might occur on direct sulfurization of the simplest hydrocarbon polymer (polyethylene) are as follows (Scheme 3): sulfur insertion into C–H bonds (*a*) to form polysulfanes **10** and polysulfide bridges **11**; hydrogen sulfide elimination (*b*) to afford polyacetylene (polyvinylene) blocks **12**; further oxidation of poly(vinylenethiol) **13** C–H bonds (*c–f*) to produce finally polythiones **14–16** or the tautomeric (*g*) form, poly(dithiolo-dithiole-3,6-diylidene) **17**; sulfur extrusion from the latter (*h*) to afford more stable poly(thienothiophene) **18** and higher polycondensed aromatic systems (*h*).



SCHEME 3

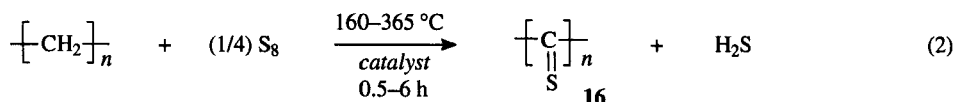
Therefore, it might be just a matter of conditions and the structure of the starting polymer to produce materials with a tailor-made combination of the polyene-polysulfide and polycondensed thiophene blocks, as well as sulfur-centered reversible redox functions. These expectations were eventually realized.

This article is a concise overview of our systematic investigation into the direct sulfuration with elemental sulfur of conventional polymers: polyethylene, polyacetylene, polystyrene, poly(5-vinyl-2-methylpyridine) and polydiethylsiloxane.

The properties of the resultant polymers elucidating their structures and potential applications such as infrared (IR), electron spin resonance (ESR) and mass spectra, conductivity, thermal and chemical stability as well as their reversible redox behavior as cathode materials in model Li cells, are briefly considered.

2. SULFURATION OF POLYETHYLENE

The reaction proceeds readily in the temperature range 160–365°C with evolution of hydrogen sulfide and, when started, continues exothermically, the reactant ratio corresponding to the exhaustive sulfuration equation (with poly(carbon monosulfide) **16** as final product) [25]:



catalyst (1 wt%): 2-mercaptobenzothiazole, diphenylguanidine, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{VO}_2\text{S}_2 \cdot \text{H}_2\text{O}$

Conventional accelerators of rubber vulcanization (2-mercaptobenzothiazole, diphenylguanidine) noticeably facilitate the reaction, decreasing its temperature and duration. The catalytic effect of cobalt dichloride and vanadyl disulfides has also been evident.

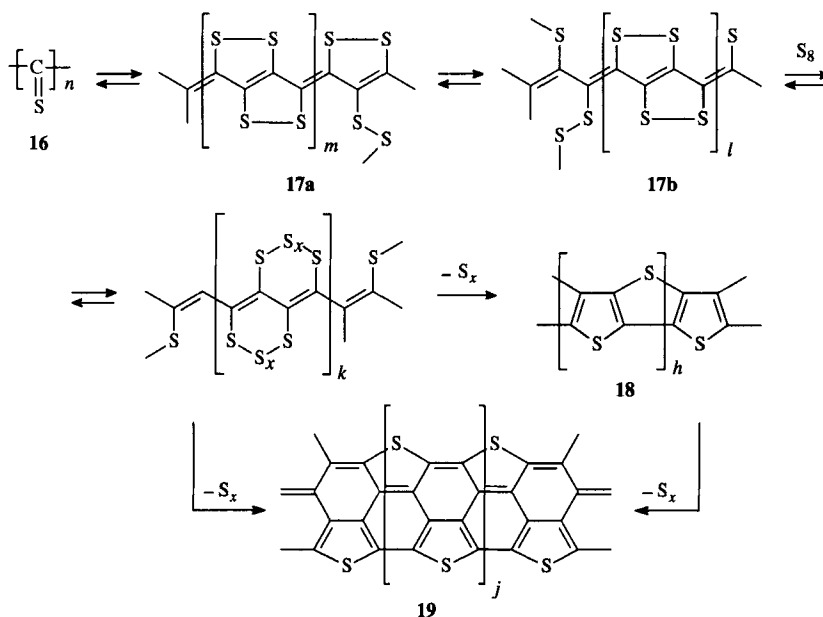
The sulfuration products are black powders with a metallic luster, insoluble in any solvent. The yields and sulfur content of the polymers depend on the reaction conditions and the kind of starting polyethylene, varying from 10 to 90% and from 20 to 80% respectively [25]. The products are mainly high ohmic semiconductors with specific electroconductivity in the range $4 \times 10^{-14} - 2 \times 10^{-9} \text{ S cm}^{-1}$ and, when doped with iodine, $2 \times 10^{-7} - 5 \times 10^{-6} \text{ S cm}^{-1}$. The X-ray patterns of the polymers exhibit some terminal reflections and point reflections from single crystals. However, they are weak and hence the materials are mainly X-ray amorphous.

Low density household polyethylene film is easily sulfured at 190–200°C for 3 h to evolve an almost stoichiometric amount of hydrogen sulfide to give a polymer in 90% yield with the sulfur content of 80%.

A longer period of heating (up to 6 h) results in a sharp decrease of the sulfur content (to 47–50%) in the final product with the hydrogen content being on the level of ~1%. These materials proved to be more stable: even multiple sulfuration of the same sample virtually does not change its composition, although its electroconductivity increases by up to 5 times, thus indicating an intensification and ordering of polyconjugation in the polymer.

On the basis of the compositions and thermal transformations and the properties of the polymers, such as IR spectra, including photoacoustic IR spectra, ESR

spectra [26], X-ray patterns, electroconductivity, differential scanning calorimetry (DSC)–thermogravimetric analysis (TGA) and cyclic voltammetry [26] data, it has been concluded [25,26] that the obtained products contain blocks of polymeric carbon sulfide **16**, its polyene–polysulfide tautomers **17**–**19** (including those with dithiolodithiole-3,6-diylidene structures **17a,b** cross-linked by di- and polysulfide bonds), ladder poly(thieno[3,2-*b*]thiophene) **18** and related parquet poly(naphthothienothiophene) blocks **19** (Scheme 4).



SCHEME 4

The DSC curve of a representative sample (Figure 1a) with the sulfur content corresponding roughly to a 1:1 mixture of the poly(thienothiophene) **18** and poly(naphthothienothiophene) **19** structures (S content 49.6%) demonstrates that the polymer is stable up to $\sim 480^\circ\text{C}$. Only a weak endothermic peak (at $\sim 380^\circ\text{C}$) is detected, which is most likely due to the cleavage of residual C–H and S–S bonds.

At the same time, the sample with a higher content of sulfur (64%) gives two exothermic peaks (at 407 and 443°C), supporting the expected rearrangement (with sulfur extrusion) of polyene–polysulfide blocks to more stable fused poly(thienothiophene) **18** and poly(naphthothienothiophene) **19** structures (Figure 1b) [25].

Generally, the products are unusually stable compared with known polymers with high sulfur content. According to TGA, the polymers consisting of poly(thienothiophene) and poly(naphthothienothiophene) blocks (sulfur content $\sim 50\%$), when heated up to $\sim 560^\circ\text{C}$ within 1 h lose only $\sim 15\%$ of their mass [25].

The mass spectra of the thermodestruction products ($40\text{--}450^\circ\text{C}$) of the sample of doubly sulfurized polyethylene (S content 49.6%) contain a peak with $m/z = 64$ attributable to disulfur (S_2), implying sulfur extrusion.

The ESR signals of the polymers are intense symmetric narrow ($\Delta H = 0.53\text{--}0.60\text{ mT}$) singlets with g factors close to that of the free electron (Table I). These characteristics

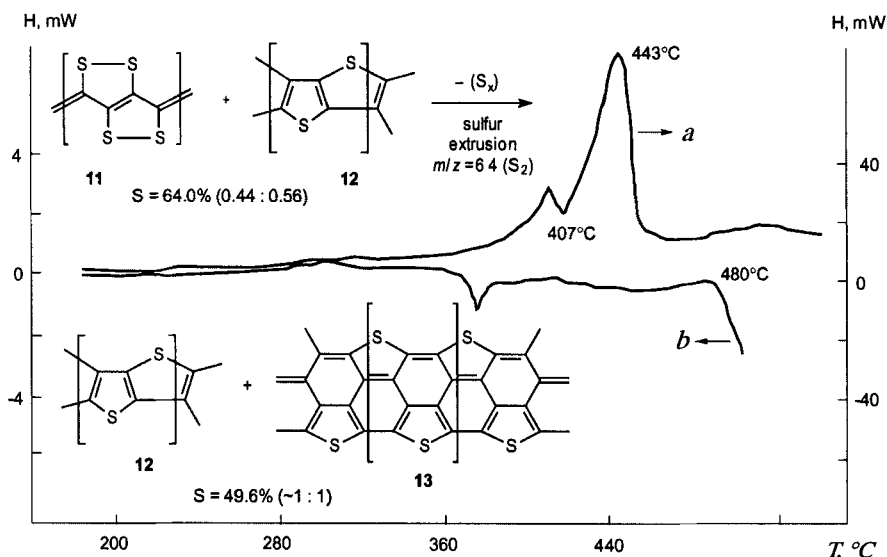


FIGURE 1 Typical DSC curves of two different samples of doubly sulfurized polyethylene.

TABLE I ESR spectra of sulfurized polyethylene [26,27]

S (%)	Concentration of spins (spins g ⁻¹)	g	ΔH (mT)
64.0	2.2 × 10 ¹⁹	2.0041	0.60
42.7	6.7 × 10 ¹⁹	2.0041	0.62
47.3	8.6 × 10 ¹⁹	2.0045	0.53
47.9	9.7 × 10 ¹⁹	2.0045	0.57

and the high concentration of paramagnetic centers confirm that the polymers contain a developed system of conjugated bonds, which is in keeping with the assigned structures [26,27].

The redox properties and electrochemical activity of the polymers and the possibility of using them as active cathode materials in lithium rechargeable batteries were studied by cyclic voltammetry (Figure 2) [26,27]. Two cathodic peaks at 2.4 and 1.9 V and one anodic peak at 2.4 V in the cyclic voltammograms are typical of polysulfide cycling [28] and confirm that the polymers do contain redox-active blocks with S–S bonds, most probably polyene–polysulfide chains.

The specific capacity of the discharge–charge process correlates with the sulfur content in the polymers and reaches its height for the most sulfurized sample (Figure 2, Table II).

The discharge characteristics of cathodes based on the polymers demonstrate their capability for multiple cycling (Figure 2, Table II).

Chemical reduction of the sulfurized polyethylene by sodium or its reaction with sodium amide in liquid ammonia leads to its partial desulfurization (e.g. from 80 to 41–45%), corresponding to the preferential formation of the more stable poly(thi-enothiophene) **18** and poly(naphthothienothiophene) **19** structures, evidently as a result of the nucleophilic cleavage of the S–S and C–S bonds followed by aromatization, including that during hydrolysis of intermediates (Scheme 5) [26].

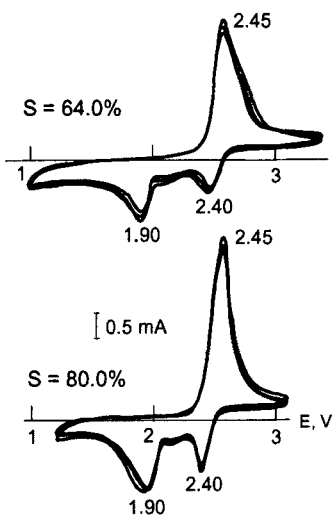
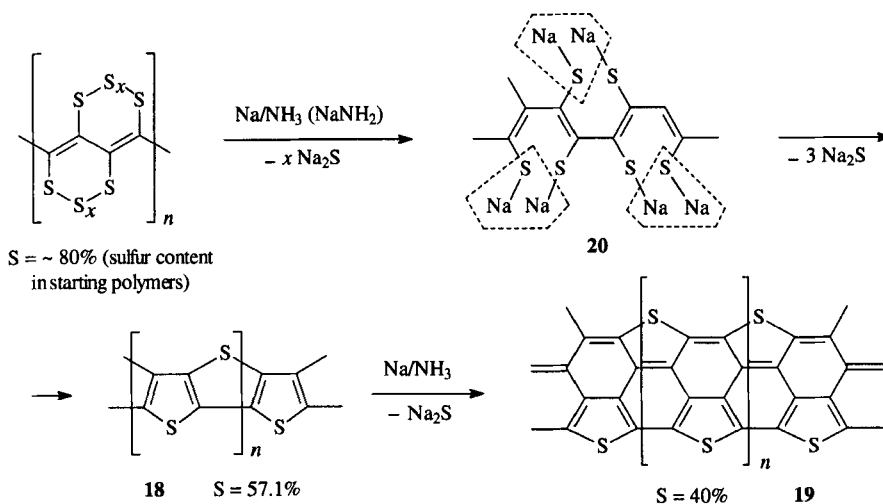


FIGURE 2 Cyclic voltammograms of sulfurized polyethylene.

TABLE II Specific capacity Q (mA h g^{-1}) of the lithium accumulator cathode (50% of the sulfurized polyethylene) [26,27]

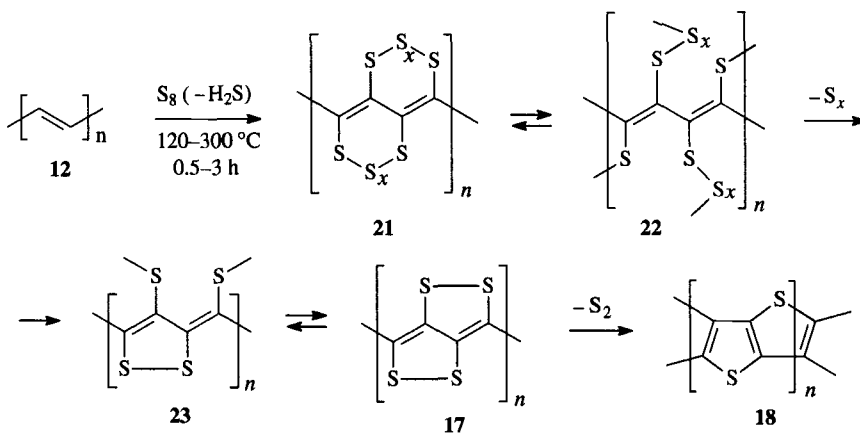
S (%)	Cycles					
	Discharge			Charge		
	1	2	3	1	2	3
80.0	400	305	280	340	330	300
64.0	240	235	230	330	310	295
49.6	110	100	90	100	90	90

Electrolyte: $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, 1 M, in a mixture of 1,3-dioxolane and 1,2-dimethoxyethane.

SCHEME 5

3. SULFURIZATION OF POLYACETYLENE

The reaction is carried out in the temperature range 120–300°C for 0.5–3 h (Scheme 6) [29]. The reactant ratio corresponds to 1–2 sulfur atoms per carbon atom. The sulfurization of polyacetylene **12** proceeds much more easily than that of polyethylene: the hydrogen sulfide evolution starts from 120°C. No catalyst is needed. The yields range from 63 to 96%.



The polyvinylene blocks **12** are expected intermediates in the polyethylene sulfurization (Scheme 3). Therefore it is not surprising that the products are similar to those obtained from polyethylene: the same black lustrous (shining like metal) powders with sulfur content from 56 to 80% [29]. Their IR spectra are also similar: there are absorption bands at 459–468 cm^{-1} and 516–598, 652–734 cm^{-1} corresponding to S–S and S–C bonds respectively, as well as the weak maxima at 1055–1061 and 1420–1570 cm^{-1} attributable to the thienothiophene framework vibrations. The broad absorption in the region of 1627–1639 cm^{-1} is typical of the polyvinylene chain. Undoped polymers [29] possess electronic conductivity in the range 1.0×10^{-15} – $0.7 \times 10^{-12} \text{ S cm}^{-1}$.

The polymers are paramagnetic with the spin concentration spanning the 2.4×10^{17} – $1.7 \times 10^{19} \text{ spin g}^{-1}$ range. Their ESR singlets, unlike the narrow symmetrical lines typical of polyvinylene, are broad and asymmetric. The g factors differ from the typical spin value (2.0023) and, for the samples with higher spin concentration, a stronger dependence on the spin–orbital contribution is observed [29].

These properties as well as their reversible redox behavior (see below) allow us to infer that polyacetylene, when heated with elemental sulfur, undergoes the same processes observed for polyethylene: dehydrogenation through the sulfur insertion into C–H bonds to release hydrogen sulfide further, forming polyvinylenes **21–23** with interchanging polysulfide moieties capable of both ring closing and cross-linking owing to the lability of the S–S bonds (Scheme 6).

A prolonged heating results in sulfur extrusion and reorganization to the poly(dithiolo-dithiole) **17** and finally to poly(thienothiophene) **18** blocks. Thus, the real materials represent a combination of all these structures including elemental sulfur, evidently in its polymeric modifications. The ratio of these blocks is determined by the reaction conditions and the further work-up.

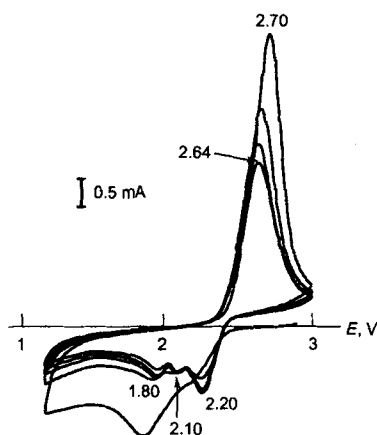


FIGURE 3 A typical cyclic voltammogram of sulfurized polyacetylene.

TABLE III Discharge capacity (mA h g^{-1}) of the lithium accumulator with the cathode containing 50% of the sulfurized polyacetylene [29]

S (%)	Cycles			
	1	5	15	25
67.0	940	505	420	370
78.0	917	480	360	350
80.0	950	490	420	400

The cyclic voltammograms of the model lithium cell cathodes based on the sulfurized polyacetylene resemble those of sulfurized polyethylene (Figure 3) [29]. On the first cycle, there are two cathodic (2.20 and 1.8 V) and one anodic (2.70 V) maxima. On cycling, the shape of the cathodic peaks changes: they sharpen and shift to a higher potential and a third peak (at 2.10 V) appears with the total specific capacity being noticeably dropped (Table III). The shape of the anodic peak does not change, but it shifts to a lower potential (2.64 V). The shape changes and shifts, as well as the fading of the capacity, indicate a structural reorganization of the material to form a highly reversible redox polymer and less soluble lithium sulfide. The latter process as well as disordering the cathode morphology [28] is probably responsible for the capacity drop at the beginning of cycling.

As a rule, the specific discharge capacity of the cathode made of the synthesized materials correlates with the sulfurization degree: the higher the sulfur content in the polymer, the longer and the more stable is the observed cycling of the cathode, although this is not always the case and sometimes exceptions occur (Table III). However, generally, the correlation is satisfied more often than not. For example, the capacity of the cathode from the polymer with a S content of 80% exceeds that with a S content of 57 by 85% for the 25th cycle (Figure 4) [29].

On the discharge curves (Figure 5) of the first cycle, this dependence of discharge capacity on the sulfur content in the cathode composition is explicitly manifested by a lengthening of both parts of the curves corresponding to the cathodic peaks.

Thus, the deep sulfurization of polyacetylene affords new electroactive polymers, with potential as high capacity cathode materials for rechargeable lithium cells.

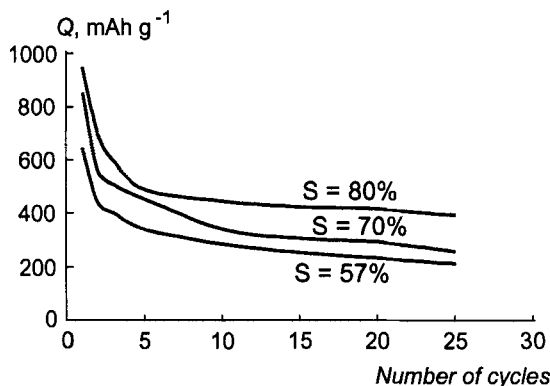


FIGURE 4 Sulfurized polyacetylene cathode cycling in a model lithium rechargeable cell.

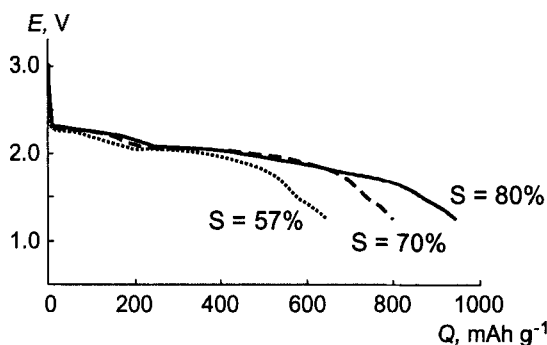


FIGURE 5 The first cycle discharge curves of the sulfurized polyacetylene in a model lithium rechargeable cell.

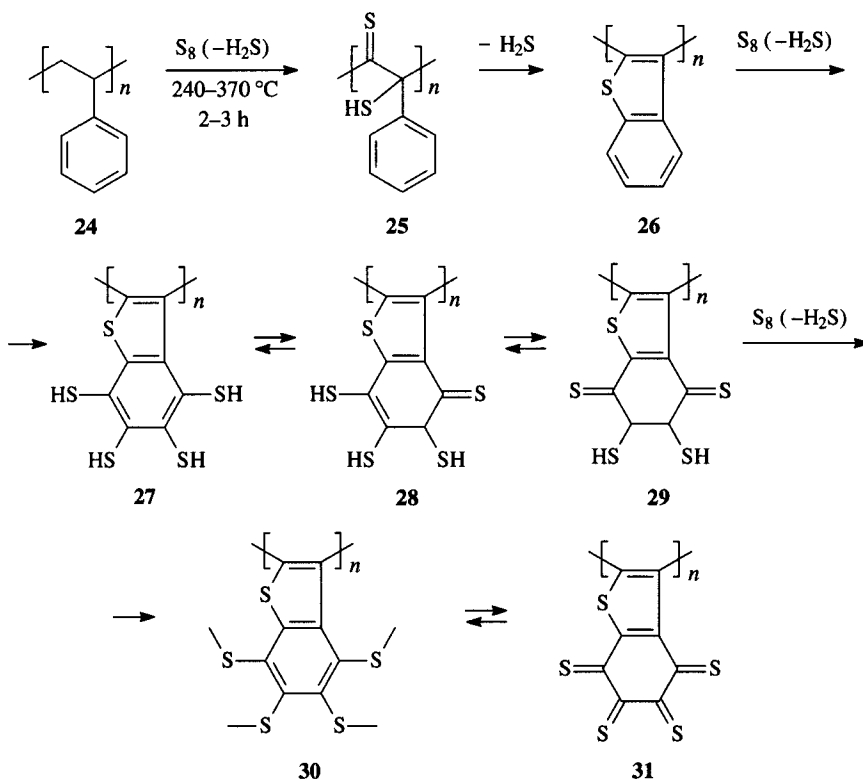
4. SULFURIZATION OF POLYSTYRENE

Direct sulfurization of polystyrene **24** with elemental sulfur (Scheme 7) [30] takes place at 240–370°C during 2–3 h with liberation of hydrogen sulfide to afford polymers containing 60–67% of sulfur (for the ideal structures **27–31** it should be ~62%). The yields range from 47% to almost quantitative. The products are insoluble black powders with metallic luster possessing conductivity $\sigma = 2.1 \times 10^{-2} - 2.1 \times 10^{-7} \text{ S cm}^{-1}$, when doped with I_2 , $\sigma = 1.2 \times 10^{-7} - 6 \times 10^{-6} \text{ S cm}^{-1}$.

No diffraction reflections are observed in the X-ray patterns of the polymers, meaning that they are X-ray amorphous.

Such catalysts as diphenylguanidine and mercaptobenzothiazole (1 wt%) promote the sulfurization to decrease the reaction temperature to 190–210°C and the reaction time to 1 h [30].

Apparently, the intermediate containing the completely sulfurized polyethylene chain **25** eliminates the hydrogen sulfide molecule to afford poly(benzothiophene) **26**. Then the benzene ring is sulfurized to yield finally cross-linked or non-cross-linked poly(4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl) **30, 31** via intermediates **27–29** (Scheme 7).



SCHEME 7

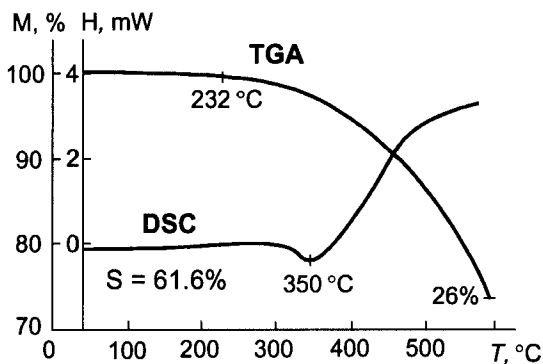
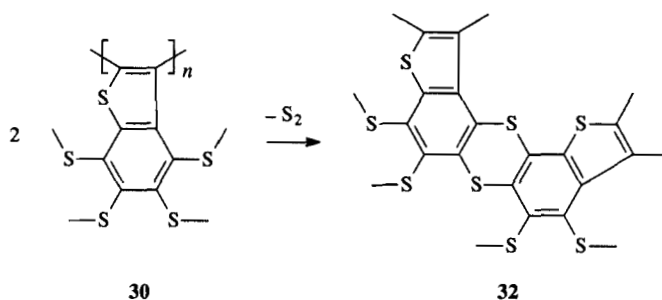


FIGURE 6 Thermal behavior of sulfurized polystyrene.

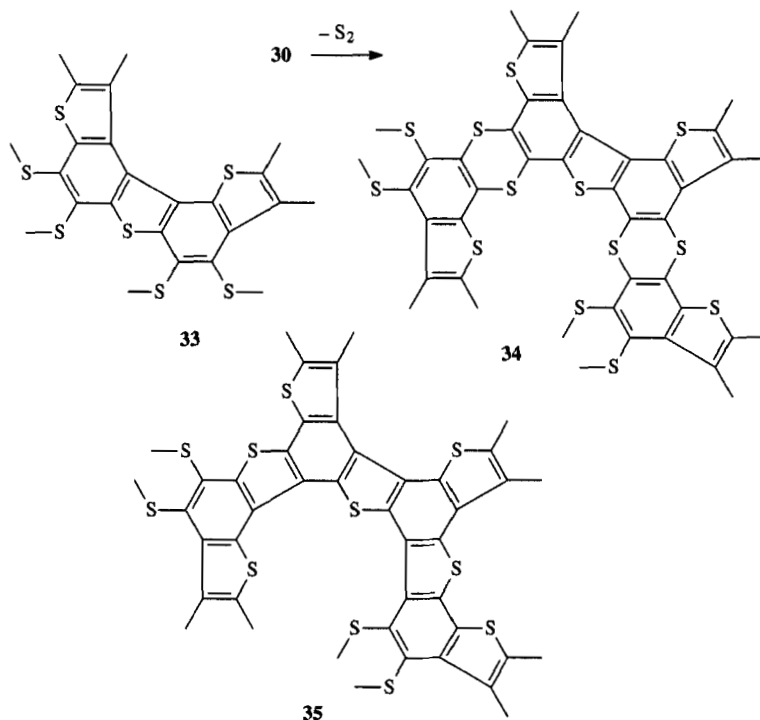
A typical DSC curve of the polymers (Figure 6) shows a weak endothermic effect at $\sim 350^\circ\text{C}$ followed by a steep exothermic elevation in the range $350\text{--}600^\circ\text{C}$ that is attributable to the initial cleavage of the S-S bond (the endothermic process) accompanied by further aromatization with the disulfur extrusion (from the two elementary units) to multiply fused blocks **32** with a decreased sulfur content (from 62.5 to 57.2%) (Scheme 8).



SCHEME 8

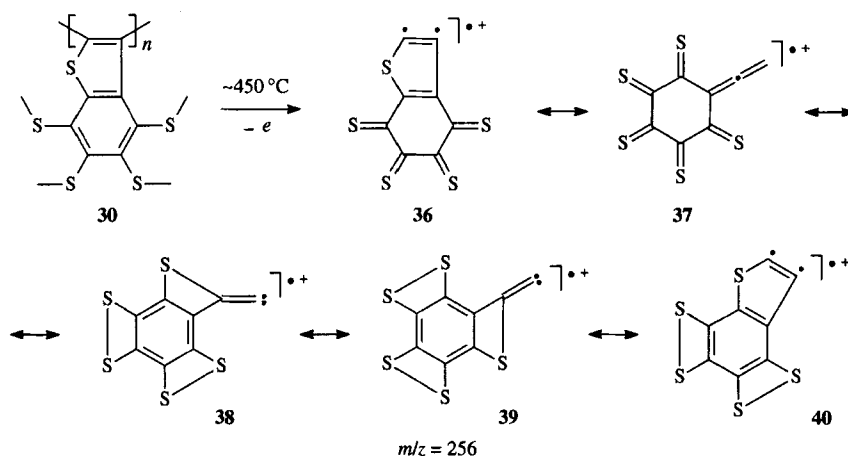
The TGA curve (Figure 6) confirms that the polymers lose up to 26% of their mass in this temperature range, thus being amazingly stable relative to conventional sulfur polymers.

Elimination of two sulfur atoms from one elementary unit of the polymer **30** results in the formation of poly(thiophenobenzothiophene) cross-linked structures **33–35** (Scheme 9) with a mass loss of 25%, which is almost exactly equal to the value determined from the TGA curve obtained on heating the sample to $\sim 590^\circ\text{C}$ during ~ 1 h [30].



SCHEME 9

At $\sim 450^\circ\text{C}$, the mass spectra of decomposition products have the most intense peak at $m/z = 256$. This mass ratio corresponds exactly to the ionized monomer 4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl **36** with the dehydrothiophene entity, a product of polymer depolymerization (Scheme 10) [30].



SCHEME 10

This radical cation (ionized biradical **36** or vinylidene carbene **37**) may be stable owing to the resonance aromatic stabilization (**36** \leftrightarrow **37** \leftrightarrow **38** \leftrightarrow **39** \leftrightarrow **40**). A structurally similar radical cation was observed previously by Fanghanel and co-workers while investigating benzenehexathiolate derivatives [31]. It is conceivable that the thermolysis of the polymer **30** and related structures can be further developed as a facile route to unique unstable molecules with the dehydrothiophene entity of the type **36**.

In the IR spectra of the polymers (Figure 7), an intense broad absorption band at 447 cm^{-1} of the S–S bond predominates. The maxima at $1503\text{--}1361\text{ cm}^{-1}$ are attributable to skeletal vibration of the exhaustively sulfurized benzothiophene core. The band at 1108 cm^{-1} corresponds to the C=S vibrations and the triplet at 850 , 790 and 735 cm^{-1} is assigned to the mixed vibrations of the aromatic C–C and C–S bonds [30].

The photoacoustic IR spectra (Figure 7) of the polymers reveal that the molecular structure of their surface layer differs from that in the bulk and mainly consists of polyfused benzothiophene blocks with reduced content of S–S and C–S bonds [30].

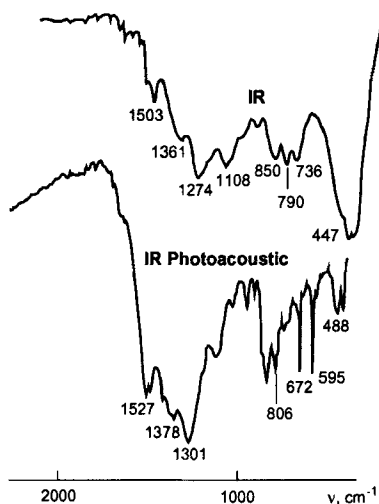


FIGURE 7 IR and IR photoacoustic spectra of the sulfurized polystyrene.

Energy-dispersive X-ray spectroscopy confirms the higher carbon content (68.8–81.3%) and the lower sulfur content (18.7–31.2%) in the surface layer of the polymers (up to 1 μm) as compared with the bulk [30]. The solid state ^{13}C nuclear magnetic resonance (NMR) spectra of the polymers have a broadened singlet at $\delta = 131$ ppm typical of polycondensed aromatic compounds [30]. The conducting electron-rich surface layer of the polymer particles may play the role of a membrane penetrable by Li^+ cations and a blocking area for thiolate anions. Such a gradient architecture of the polymer nanoparticles should secure longer cycling owing to a better prevention of the contact with the Li metal anode.

All samples of the sulfurized polystyrene are paramagnetic [27,30]. Their ESR spectra have intense symmetric narrow ($\Delta H = 0.36\text{--}0.46$ mT) singlets with g factors similar to that for the free electron (Table IV). These features and the high concentration of unshared spins are in agreement with an extensive system of conjugated bonds in the polymers.

In cyclic voltammograms of the polymers (Figure 8), two pronounced cathodic peaks (at 1.98 and 2.38 V) and one anodic peak (at 2.40 V) are observed, confirming the presence of redox-active S–S bonds. The discharge capacity of the lithium cell cathode with 50% of the polymer was 330 mA h g^{-1} at stable cycling [27,30].

On the basis of the elemental analysis, IR, photoacoustic IR, NMR and ESR spectra, mass spectrometry, X-ray diffraction, energy-dispersive X-ray spectroscopy and DSC–TGA data, conductivities, results of chemical reduction and the character of electrochemical behavior, it is concluded that the exhaustively sulfurized polystyrene has primarily the cross-linked poly(4,5,6,7-tetrathiono-4,5,6,7-tetrahydrobenzothiophene-2,3-diyl) structure **30** [30].

Double sulfurization or reduction with lithium of the polymers leads to their partial desulfurization to more stable multiply fused ladder and parquet poly(benzothiophene) structures.

TABLE IV ESR spectra of sulfurized polystyrene [27,30]

S (%)	Concentration of spins (spins g^{-1})	g	ΔH (mT)
42.1	5.0×10^{19}	2.0044	0.44
53.0	6.6×10^{19}	2.0042	0.36
55.9	13.0×10^{19}	2.0040	0.46
66.0	7.3×10^{19}	2.0041	0.36

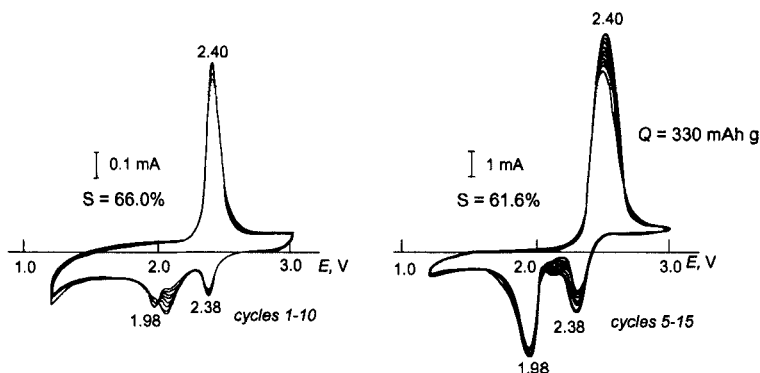


FIGURE 8 Cyclic voltammograms of sulfurized polystyrene.

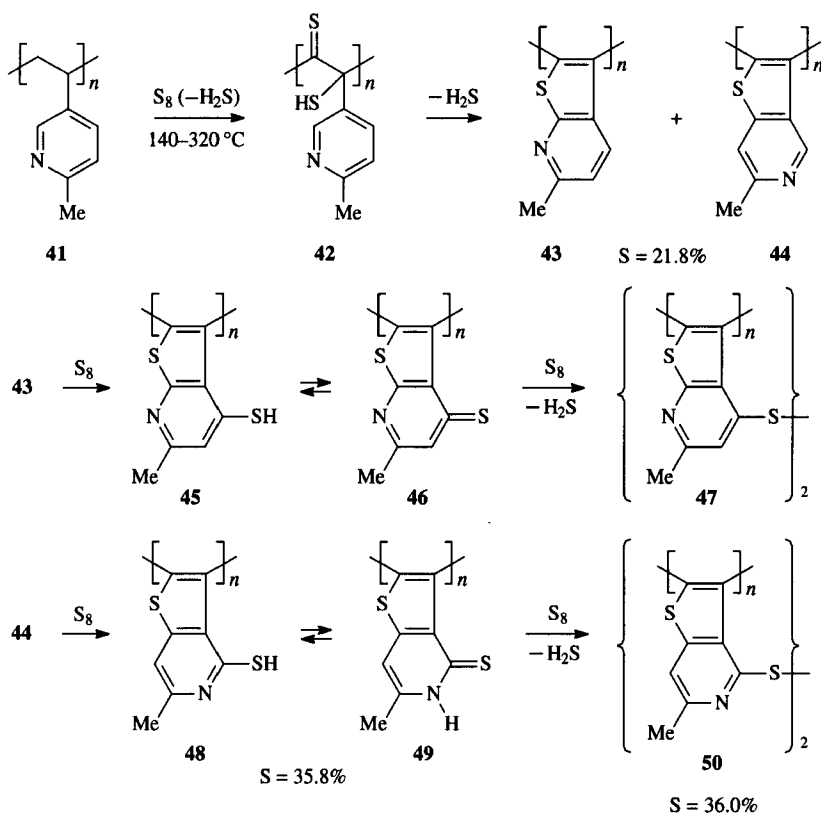
5. SULFURIZATION OF POLY(5-VINYL-2-METHYLPYRIDINE)

The reaction of poly(5-vinyl-2-methylpyridine) **41** with elemental sulfur is carried out at 140–320°C and various ratios of reactants (from 12.5 to 49.6 g-atom of sulfur per monomeric unit) during 2–7 h [32,33].

The products are mostly insoluble black metal-like lustrous powders with sulfur content within 16–45% and conductivity within 6×10^{-11} – $1.6 \times 10^{-7} \text{ S cm}^{-1}$. Diffraction reflections are not observed in the X-ray patterns of the polymer powders, indicating the X-ray amorphous structure of the products. Yields range from 58 to 91%.

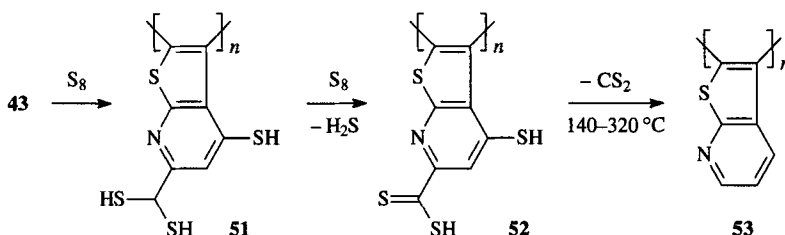
A one-step sulfurization affords up to 36% of sulfur in the product, which corresponds to two sulfur atoms per monomer unit. Repeated reaction with the same sample allows up to 45% of sulfur to be chemically bound by the polymer.

From the elemental analysis and IR spectra, including photoacoustic IR spectra, and from the analogy with sulfurized polyethylene and polystyrene, it follows that at first dehydrogenation of the main chain to the poly(thion-thiol) **42** occurs (Scheme 11). The latter undergoes ring closure to the structurally isomeric poly(6-methylthienopyridines), [2,3-*b*] **43** and [3,2-*b*] **44**. The second sulfur atom may be inserted into both the pyridine cycle and the methyl group. In the former case, isomeric thiols **45**, **48** and their thione tautomers **46**, **49** as well as corresponding cross-linked disulfides **47**, **50** are formed.



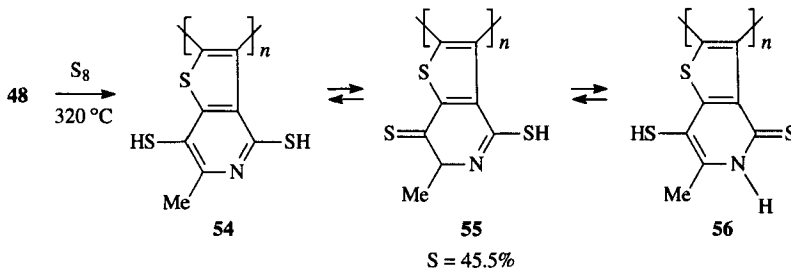
SCHEME 11

When the methyl group is sulfurized, the geminal dithiols **51**, dithiocarbonic acids **52** and their desulfurization products are possible (Scheme 12, showing several selected structures) [32].



SCHEME 12

The repeated sulfurization allows the third sulfur atom to be introduced into the polymer and the sulfur content to be increased to ~45%. Some probable structures of the doubly sulfurized polymers **54–56** are shown in Scheme 13.



SCHEME 13

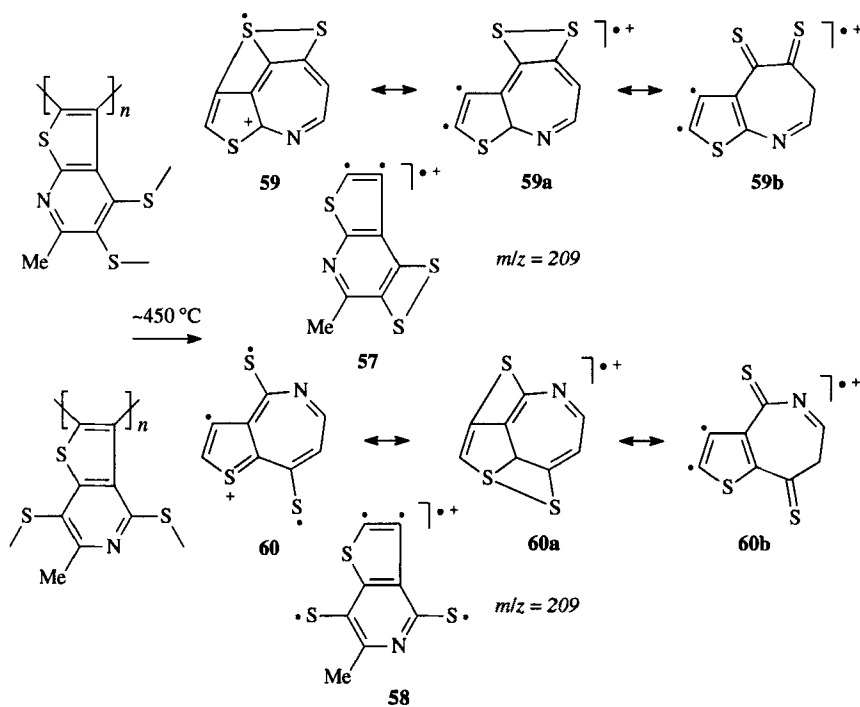
In real materials, the dithiols and their thione tautomers are obviously interlaced in an oxidized disulfide cross-linked network. Nonetheless, in the IR spectra, the characteristic bands of all structural elements of these tautomers, including thiol, thione and NH functions, are fixed [32,33].

The doubly sulfurized polymer, when studied by mass spectrometry, gives volatile products in the temperature range 250–450 °C (which agrees well with the DSC–TGA). Among the decomposition products, the most intense peak has mass number 209, which can be attributed to the thienomethylpyridinedithiyl **57**, **58** and thienoazepinedithiyl **59**, **60** radical cations with the dehydrothiophenic entities (in Scheme 14 only selected isomeric resonance forms **59a,b**, **60a,b** from any possible are shown).

The three-center S–S bond formation in polyconjugated condensed carbon–sulfur polymers like that shown in Scheme 14 has recently been supported theoretically by Hoffmann and co-workers [34,35].

The high abundance of the radical cation with mass number 209 allows us to assign it to the monomeric units of the polymer, which, therefore, are most probably the isomeric thienopyridine-dithiyls **57**, **58** and thienoazepine-dithiyls **59**, **60** [32,33]. Thus, flash pyrolysis of the sulfurized poly(vinylpyridines) may provide for a feasible technique to generate unstable and exotic intermediates such as dehydrothienopyridine

and dehydrothienoazepine species functionalized with thione groups, interesting objects for both theoretical studies and synthetic application.



SCHEME 14

Electroconducting and paramagnetic properties of the polymers match those of organic semiconductors with a developed system of conjugation (Table V). Their ESR signals are practically symmetric singlets with g factors close to that of the free electron (Table V).

As the sulfur content in the polymer increases from 16 to 31%, the conductivity grows about 3 times and the concentration of paramagnetic centers is enhanced by almost 1 order of magnitude. This may be considered as evidence that the charge carriers are mostly electrons and that a strong electron interaction of the sulfur atoms with the whole conjugated system takes place in the polymer, which is in keeping with the assigned structures. The significant increase of the conductivity (up to $1.6 \times 10^{-7} \text{ S cm}^{-1}$), while the spin concentration remains practically unchanged (Table V), implies a higher ordering of the supramolecular structure of the polymer resulting from the repeated sulfurization.

TABLE V Electroconductivity and ESR spectra of sulfurized poly(5-vinyl-2-methylpyridine) [33]

S (%)	σ (S cm^{-1})	Concentration of spins (spins g^{-1})	g	ΔH (mT)
16.1	6.4×10^{-11}	6.2×10^{18}	2.0046	0.49
31.1	1.7×10^{-10}	5.0×10^{19}	2.0043	0.56
44.9	1.6×10^{-7}	4.5×10^{19}	2.0044	0.58

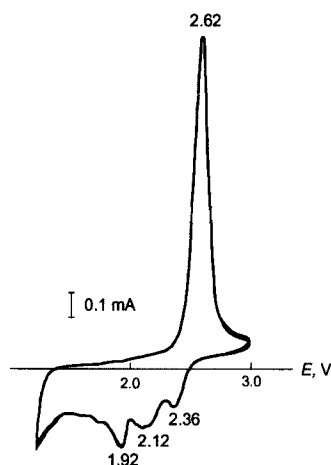
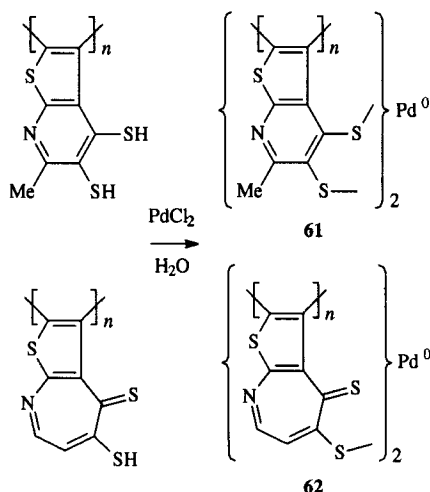


FIGURE 9 Cyclic voltammogram of sulfurized poly(5-vinyl-2-methylpyridine).

The electrochemical behavior of the doubly sulfurized samples in model lithium rechargeable cells confirms the presence of redox-active thiol, thione and disulfide functions in the polymer [33]. According to cyclic voltammograms (Figure 9), a complex multistep reduction of the polymers occurs with maxima at 2.36, 2.12 and 1.92 V, followed by oxidation at 2.62 V. These peaks are typical of redox behavior of the polymers with thiol, thione, disulfide and polysulfide structures similar to those identified in the polymers by other methods [25–27,29,30,32,33].

The polymers readily take up heavy metals such as Co, Pd and Hg from aqueous solutions of their salts and can be used as pollutant scavengers and polymer matrices for catalyst design. If the salts are chlorides, no chlorine is detected in the polymeric complexes thus formed and, in the case of palladium, the metal is in a zero-valent state, which corresponds to the expected reduction of the palladium cation with the thiol functions of the polymer (Scheme 15). In fact, the intense diffraction lines of palladium metal are observed in the X-ray patterns of the palladium complexes **61**, **62** [32].



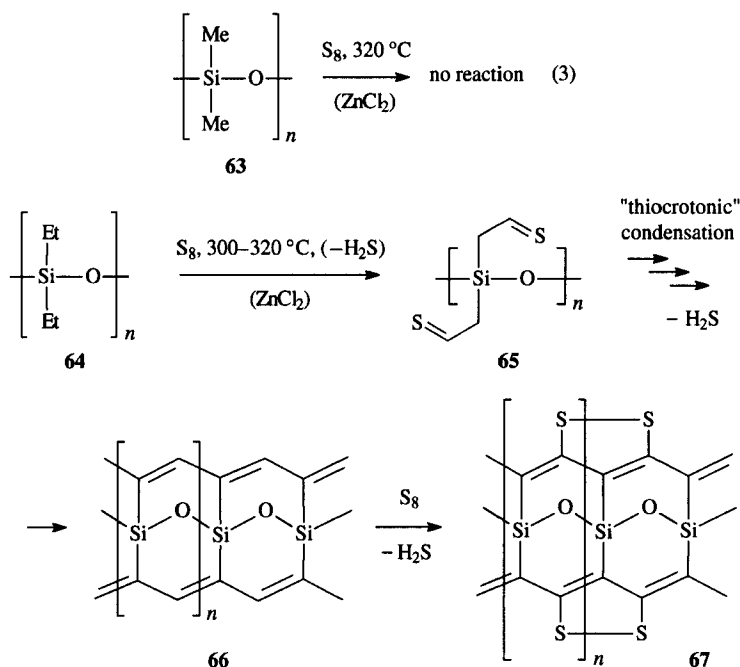
SCHEME 15

Thus, judging from the combined data of elemental analysis, IR, photoacoustic IR, ESR and mass spectroscopy, X-ray patterns, DSC-TGA, electrochemical and chemical properties, the sulfurized poly(5-vinyl-2-methylpyridine) represents a cross-linked polymer mostly consisting of isomeric poly(methylthienopyridines) and poly(thienoazines) functionalized with thiol, thione, disulfide and polysulfide groups [32,33].

6. SULFURIZATION OF POLYDIETHYLSILOXANE

While polydimethylsiloxanes **63** with different degrees of polymerization virtually do not react with elemental sulfur at temperatures up to 320°C (see equation (3)), polydiethylsiloxane **64** turns out to be more reactive in the sulfurization reaction [36].

With an excess of sulfur at 300–320°C, it is transformed within 7 h into a product insoluble in boiling benzene (the sulfur content is 32.4%), the liberation of hydrogen sulfide accompanying the reaction [36]. Under the same conditions with ZnCl₂ as a catalyst, a deeper sulfurization occurs to increase the sulfur content in the product to 38.5%. This result corresponds to the insertion of two sulfur atoms into each monomeric unit of polydiethylsiloxane (Scheme 16).



SCHEME 16

Since polydimethylsiloxane is inert under these conditions, it is reasonable to infer that in polydiethylsiloxane it is the remote methyl group that reacts with sulfur. Then the unstable polysiloxane structures **65** with thioformylmethyl groups can be intermediates, which further undergo a crotonic-like condensation to eliminate hydrogen sulfide and to form a polyvinylene entity **66**. The latter is readily oxidized by elemental sulfur (see Section 3), even under milder conditions to give polyenepoly-sulfide **67** with elimination of extra hydrogen sulfide (Scheme 16).

The final products of sulfurization are black paramagnetic powders (2×10^{18} spins g^{-1} , $g = 2.0043$, $\Delta H = 0.7 \text{ mT}$) with electrical conductivity of $4.8 \times 10^{-13} \text{ S cm}^{-1}$, and $3.2 \times 10^{-7} \text{ S cm}^{-1}$ when doped with I_2 [36].

The polymers are not hydrolyzed by a boiling 25% aqueous solution of NaOH for 5 h which indicates that they contain no Si-S bonds [37]. When they are boiled in 10% aqueous HCl (10 h), a minor amount of hydrogen sulfide is liberated and, correspondingly, the content of sulfur decreases (from 38.5 to 32.3%), which is due to the hydrolysis of residual CH=S groups in **65** and (or) intermediate structures formed during their polymerization ($> \text{CH-S-}$)_n.

In the IR spectra of the polymers, the intensity of absorption bands of the SiCH₂ group (2960, 2940, 2910, 2880, 1450, 1410, 1370 and 1240 cm^{-1}) is sharply diminished as compared with that of the starting material **64**, but a broad absorption band in the 1000–1110 cm^{-1} region characteristic of the Si-O bond remains unchanged.

The electrochemical activity of the polymers has been studied in model lithium rechargeable batteries. The cyclic voltammograms (Figure 10a) have pronounced reduction peaks at 2.4 and 1.9 V and an oxidation peak at 2.5 V typical of polysulfide chains. The polymers are capable of multiple cycling, and the specific capacities of the cathode and anode processes remain essentially stable (Figure 10b), although the capacity level is not as large as predicted from the ideal structure **67**, implying that a part of sulfur is present in the electrochemically inactive poly(thienothiophene) **18** blocks.

Thus, the character of electrochemical activity of the polymers confirms the presence of S-S bridges in their structure.

The DSC curve (Figure 11a) shows that the material contains no elemental sulfur (no endothermic peaks of sulfur melting except for moisture evaporation at 98°C). It is stable up to 390°C. At this temperature, an endothermic peak with a further sharp

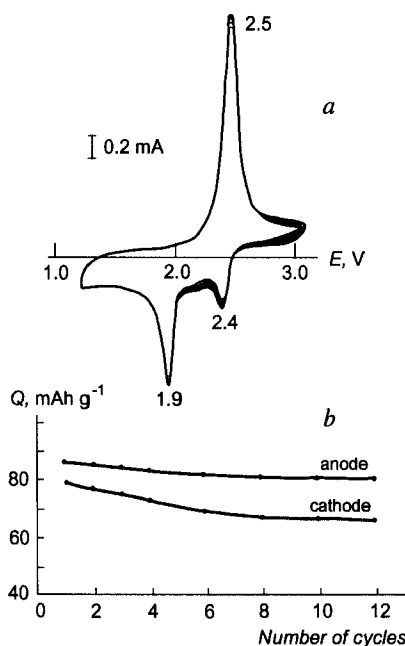


FIGURE 10 Electrochemical behavior of sulfurized polydiethylsiloxane.

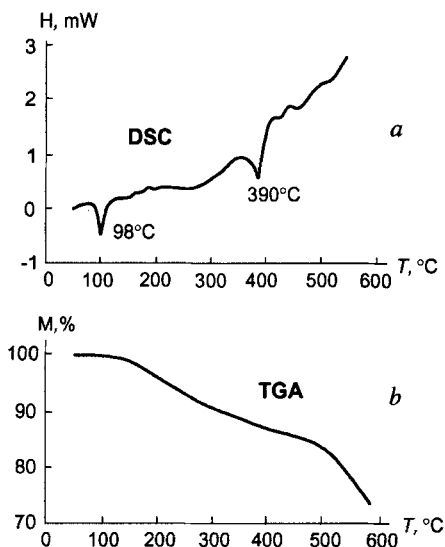


FIGURE 11 DSC and TGA curves of sulfurized polydiethylsiloxane.

exothermic elevation is observed. The picture most likely is due to the cleavage of S–S bonds with extrusion of sulfur and aromatization ('thiophenization') of the remaining structures, as observed in the sulfurized polyacetylene [29]. Indeed, from the TGA curve (Figure 11*b*) it is seen that below $\sim 490^{\circ}\text{C}$ the sample loses about 16% of its mass, which does correspond to the loss of approximately one sulfur atom per elementary unit. During further heating, the mass loss reaches $\sim 30\%$ near 600°C . This matches an almost complete desulfurization and carbonization of the polyacetylene blocks.

On the whole, the chemical, spectral, electrochemical, physical and thermochemical properties of the polymers agree with the assigned polyconjugated ladder structure **67**.

7. CONCLUSION

A new general concept for the design of electroactive and conducting materials with functionalized polyene polysulfide and polycondensed thiophene entities based on the direct sulfurization with elemental sulfur of diverse polymers has been developed. The experimental results have been presented at a number of international conferences [38–44].

The major problems to be solved before the concept can be applied in manufacturing advanced materials are a better uniformity and better-defined structures as well as the processability of the polymers. We believe that these problems can be overcome by careful optimization of the synthesis in each particular case including the correct choice of catalyst, starting polymer structure and, particularly, controlled heating to secure the solubility and meltability of the resulting products.

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