Synthesis of polyacetylene with sulfoxide functions

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Polyacetylene functionalized by sulfoxide groups was synthesized from poly(methyl vinyl sulfoxide) by the elimination of methanesulfenic acid under the action of a strong base at 20—50 °C.

Key words: poly(methyl vinyl sulfide), poly(methyl vinyl sulfoxide), desulfurization, polyacetylene.

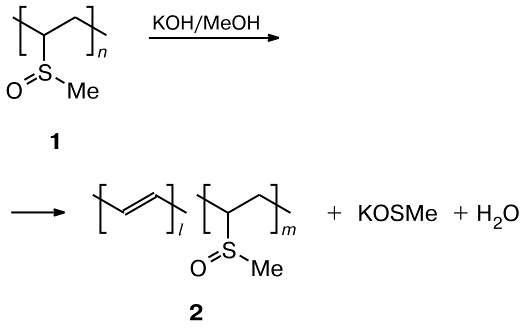
The thermal (150 °C) elimination of benzenesulfenic acid from poly(phenyl vinyl sulfoxide) is considered as a promising method for the synthesis of polyacetylene modified by sulfoxide functions.[1—6] In combination with other types of chemical modification, this method makes it possible to prepare acetylene copolymers with new surface, optical, and electronic properties. Since blocks of different nature are thermodynamically incompatible, these copolymers can exhibit the microphase separation to form paracrystalline nanostructures in the solid state and the formation of Langmuir—Blodgett films or stable self-organized micelle-like nanoparticles in solutions.[6] These new varieties of polyacetylene seem challenging as antistatic additives, homogenizing agents for polymeric mixtures, optoelectronic materials, sensors, switches, molecular conductors, and nanoelectrinic devices.[6]

In this work, we present the results of studying new routes for the synthesis of functionalized polyacetylene from poly(methyl vinyl sulfoxide) (PMSO, **1**) by a base under mild conditions at room temperature or on weak heating.

We found that polyacetylene functionalized by sulfoxide groups (**2**) is readily formed from PMSO **1** *via* the partial elimination of methanesulfenic acid under the action of a strong base at 20—50 °C.

The soluble precursor of functionalized polyacetylene is PMSO **1**. The latter was synthesized by the oxidation of poly(methyl vinyl sulfide) (PMS) with 30% hydrogen peroxide (equimolar amount of H_2O_2 based on the PMS unit, acetone—benzene (9 : 1) mixture, 60 °C, 12 h). The oxidation proceeds only to the sulfide sulfur, does not involve the main chain, and induces no destruction of macromolecules, because no decrease in the molecular weight (MW) of the modified product was observed (MW of the sulfide polymer is 15000, and MW of the sulfoxide polymer is 16300).

Scheme 1



The physicochemical properties of the starting and oxidized polymers differ strongly: their consistence (resin and power) and solubility in water change (the sulfide polymers are not dissolved in water, while the sulfoxide polymers are highly water-soluble).

The structure of the modified polymers was found by analysis of the IR and ^{1}H NMR spectra.

The IR spectrum of the oxidized polymer exhibits a very strong band of stretching vibrations of the S=O bond at 1030 cm^{-1}; absorption bands at 1290 cm^{-1} and 1120 cm^{-1} are attributed to vibrations of the SO_2 bonds, and the non-oxidized sulfide C—S bonds appear as a weak band at 680 cm^{-1}.[7,8]

The ^{1}H NMR spectra of PMSO (DMSO-d_6) contain signals of Me groups of three types: the sulfide type at 1.89 ppm, sulfoxide at 2.07 ppm, and sulfone at 2.39 ppm; in addition, the spectrum contains a broad signal at 3.04 ppm corresponding to protons of the CH and CH_2 groups of the polymeric chain. According to the NMR spectroscopic data, under the accepted oxidation conditions, the content of the sulfoxide blocks in the oxidized polymer, which is a unique triple copolymer, is 70 mol.%,

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and that of the sulfide and sulfone blocks is 13 and 17%, respectively.

The treatment of this polymer with a methanolic solution of KOH results in the elimination of the lateral sulfoxide groups to form functionalized polyacetylenes with different compositions. The structure of the synthesized polymeric products is confirmed by their analytical and spectral (IR, ESR) characteristics (Tables 1 and 2).

The IR spectrum of the functionalized polyacetylene[8] has a high background characteristic of polyconjugated polymers, its broad band of stretching vibrations at 1640—1670 cm^{-1} corresponds to polyenic blocks, the intensity of the band of the S=O bonds at 1030 cm^{-1} is strongly decreased, and the absorption bands of SO_2 appear at 1290 and 1120 cm^{-1}.

The NMR method cannot be used for analysis because of a low solubility of functionalized polyacetylenes.

Table 1. Synthesis of functionalized polyacetylenes (PA) from poly(methyl vinyl sulfoxide) (50 °C, EtOH, 1 h)

Sample	KOH (wt.%)	Found (%)				Y[a] (mol.%)	
		C	H	S	K	PA	PMSO
1[b]	No	41.74	7.82	32.41	No	—	—
1	10	45.99	7.26	28.14	0.78	48	52
2	40	46.89	7.45	25.32	0.60	59	41
3	40[c]	46.14	7.33	25.71	0.65	57	43
4	50[d]	49.41	7.26	24.52	0.74	61	39
5	50	50.64	7.65	23.82	0.56	64	36
6	60[d]	52.30	8.16	23.14	0.49	65	35
7	60	54.12	7.49	22.71	0.65	67	33
8	60[e]	56.50	7.28	19.12	0.77	75	25

[a] Y is the calculated content of blocks in the modified polymer.
[b] Starting PMSO.
[c] In argon.
[d] 40 °C.
[e] 20 °C, 30 h.

Table 2. Characteristics of the ESR spectra of functionalized polyacetylenes

C_S (%)	$C_{p.c}$ cP/g	*g* Factor	ΔH/Oe
28.14	$1 \cdot 10^{16}$	2.006	10
25.32	$4 \cdot 10^{16}$	2.006	11
24.52	$6 \cdot 10^{16}$	2.005	9
23.14	$2 \cdot 10^{17}$	2.005	10
22.71	$4 \cdot 10^{17}$	2.005	11
20.04	$1.0 \cdot 10^{18}$	2.005	10
19.12	$1.2 \cdot 10^{18}$	2.008	8

Note. C_S is the sulfur content in the sample, and $C_{p.c.}$ is the concentration of paramagnetic centers.

The ratio of the polyacetylenic to sulfoxide blocks in the copolymer can be controlled by the variation of the reaction conditions: the reaction durability and temperature and the amount of a base taken for elimination (see Table 1).

In this case, the main factor is the KOH concentration in the reaction mixture. The maximum content of acetylenic blocks in the modified copolymer is 48 and 75% at 10 and 60% KOH, respectively.

The change in the content of the polyacetylenic blocks and, correspondingly, in the conjugation lengths is confirmed by the ESR spectral data for the polymers obtained under different elimination conditions (see Table 2).

The ESR signals are asymmetric and narrow singlets of different intensities with close *g* factors (the region of free radicals) caused by polyconjugated structures. The concentration of the paramagnetic centers is characteristic of polymers with a conjugation system. The asymmetry of signals can be related to both sulfur atoms in macromolecules and the heterogeneous composition of the macromolecules, whose paramagnetic centers have different but close *g* factors (see Table 2).

Thus, taking into account that the precursor poly(methyl vinyl sulfoxide) is accessible, its desulfurization temperature is low (unlike the known thermal process that occurs at 150 °C), and the copolymer composition can easily be controlled by a change in the modification conditions, we can conclude that the proposed approach substantially extends and supplements the available arsenal of methods for polyacetylene functionalization.

Experimental

IR spectra of the synthesized samples were recorded on Bruker IFS 25 instruments in a microlayer or KBr pellets. ^1H NMR spectra were obtained on a Bruker DPX 400 spectrometer (400 MHz) in DMSO-d_6 with water signal decoupling using HMDS as the standard. ESR spectra of solid powders were recorded at room temperature on an SE/X-2547 spectrometer (Radiopan, Poland).

The molecular weight of polymers was determined by the isopiestic method in benzene.[9]

Poly(methyl vinyl sulfoxide) **1** was synthesized by the oxidation of poly(methyl vinyl sulfide).

Methyl vinyl sulfide (purity 99.9%) was synthesized according to a previously described method[10,11] and purified by fractionation. The monomer purity was monitored by GLC (LKhM-80 chromatograph, katharometer as the detector, column 1 m×4 mm packed with 15% Carbowax 20M on Cromaton-N-AW-DMCS, temperature of the evaporator 180 °C, helium as the carrier gas). The constants of the monomer corresponded to published data[12]: b.p. 64 °C (720 Torr), n_D^{20} 1.4843, and d_4^{20} 0.9026.

Methyl vinyl sulfide was polymerized in ampules under argon by the action of 1% AIBN (60 °C, 30 h). The resulting polymer was precipitated from benzene to methanol and dried *in vacuo* (1 Torr) to a constant weight. The yield of PMS was 75% (dense, colorless, and transparent resin insoluble in water and well soluble in benzene and chloroform, MW 15000.

Found (%): C, 48.65; H, 8.11; S, 43.24. Calculated (%): C, 48.60; H, 8.15; S, 43.25.

Synthesis of poly(methyl vinyl sulfoxide) (1) (general procedure). A 35% solution of H_2O_2 (4.4 mL) was slowly added dropwise with stirring to a solution of PMS (4.2 g, 56.6 mmol) in acetone (37.8 mL) and benzene (4.2 mL), while the temperature was maintained at 20 °C by external cooling. After this the reaction mixture was stirred at 60 °C for 12 h (reflux condenser). Then organic solvents were distilled off, water was removed by azeotropic distillation with benzene, and the polymer was dried *in vacuo* to a constant weight (1 Torr, 6 h). As a result, PMSO was obtained (4.9 g) as a yellow powder soluble in DMSO, water, methanol, and ethanol (MW 16300). Found (%): C, 41.74; H, 7.82; S, 32.41. Calculated (%): C, 39.97; H, 6.71; S, 35.57 (the enhanced content of carbon and hydrogen along with the lowered sulfur content in the polymer is caused, most likely, by the partial elimination of methanesulfenic acid already during the synthesis).

Synthesis of functionalized polyacetylene (2). A solution of KOH (1.24 g, 22.2 mmol) in methanol (1.24 g) was added with stirring at room temperature to a solution of PMSO (2.0 g, 22.2 mmol) in ethanol (10 mL). The mixture of reagents blackens and after 30 h transforms into a gel. At 50°C gel formation occurs already after 20—25 min.

The reaction mixture was evacuated (1 Torr, 5 h), and the gel transformed into a brittle polymer, which was powdered and washed with water and ethanol to the neutral reaction. After drying *in vacuo* to a constant weight, we obtained a black brittle powder-like polymer insoluble in organic solvents (1.18 g). Found (%): C, 56.50; H, 7.28; S, 19.12; K, 0.77. Calculated (for the polymer containing 70 mol.% acetylenic blocks and 30 mol.% methyl vinyl sulfoxide blocks) (%): C, 59.11; H, 7.08; S, 22.54.

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