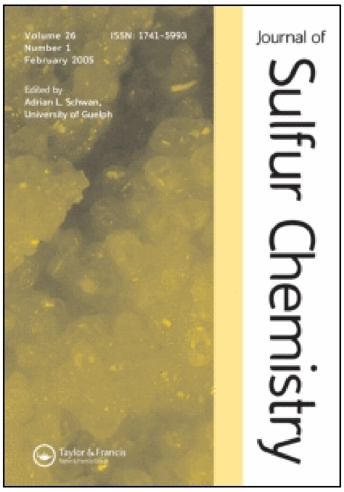

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Polysulfoxides: Synthesis, Properties, and Applications

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POLYSULFOXIDES: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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This review covers the synthesis, properties, and applications of high-molecular polysulfoxides and their copolymers, which have been intensively studied in recent years. The synthesis of polysulfoxides by radical and ionic polymerization, polycondensation, and by polymer modification are discussed. Some fields of polysulfoxide application are considered.

Key words: Polysulfoxides, polymerization, polycondensation, polymer modification

INTRODUCTION

During the last decade polymers containing sulfoxide groups have attracted growing attention of research workers owing to certain unique properties of sulfoxides. Thus, they have turned out to be excellent extractants for metal salts and antibiotics, they are applied to organic synthesis, they appear in the role of physiologically active substances, etc. Thus, well-justified special emphasis has been given to investigations of the properties and behavior of sulfoxide-containing polymers in reactions where low-molecular sulfoxides have proved to be specially interesting. Some extant reviews concerned with the preparation and application of polysulfoxides[1-3] do not claim to cover the literature *in toto*. The presented paper is intended to summarize and systematize the data and results obtained so far. The preparation of polysulfoxides, their properties, and their potential applications are reviewed below.

PREPARATION OF POLYSULFOXIDES

Polymers containing sulfoxide groups may be obtained by any of the known methods, *i.e.* by polymerization, by polycondensation, and by modification of macromolecular compounds containing a variety of functional groups.

Polyaddition and Polycondensation

Until recently all attempts to homopolymerize vinyl sulfoxides in the presence of radical initiators were failures irrespective of the initiators and conditions employed.[2,4-6] The sulfoxide group was believed to inhibit radical processes. However, the present authors[17] succeeded in obtaining a methyl vinyl sulfoxide (MVSO) low-molecular homopolymer ($\ln \eta_r/c = 0.07$) in the presence of azobisisobutyronitrile (AIBN) in bulk and in aqueous medium. However, no corresponding success was achieved in preparing homopolymers based on ethyl vinyl sulfoxide (EVSO), butyl vinyl sulfoxide (BVSO), and *t*-butyl vinyl sulfoxide, respectively, under analogous conditions. The failure of EVSO and BVSO to homopolymerize was attributed to an increasing chain transfer constant with respect to the sulfoxide group with growing size of the substituent (Table 1).[8,9]

Table 1. Chain transfer constants (C_s) in methyl methacrylate polymerization (AIBN) in R_2SO

R_2SO	$C_s \cdot 10^5$	Ref.
dimethyl sulfoxide	0.75	8
diethyl sulfoxide	5.75	8
dibutyl sulfoxide	60.0	8
dihexyl sulfoxide	100.0	9
dicyclohexyl sulfoxide	500.0	9
diphenyl sulfoxide	600.0	9
dibenzyl sulfoxide	2200.0	9

In copolymerizations vinyl sulfoxides react with a number of vinyl monomers.[4,7,10,11] The resonance stabilizations (Q) and the polar (ē) factors lie in the range 0.05–0.1 and 0.6–0.9, respectively, as calculated for vinyl sulfoxides based on the data given in Table 2.[12] The positive value of the polar factor is due to the electron-acceptor character of vinyl sulfoxides. The low value of the resonance stabilization factor shows the absence of conjugation (or the presence of a rather small one) between the vinyl and sulfoxide groups.

Table 2. Copolymerization constants of vinyl sulfoxides (M_1) with vinyl monomers (M_2)

M_1	M_2	r_1	r_2	Ref.
MVSO	styrene	0.01	4.2	4
MVSO	vinyl acetate	2.23	0.09	7
EVSO	styrene	0.02	7.0	5
EVSO	methyl methacrylate	0.01	10.0	5
EVSO	acrylonitrile	0.2	3.0	5
EVSO	vinyl acetate	3.4	0.11	7
BVSO	styrene	0.02	7.21	10
BVSO	methyl methacrylate	0.02	10.2	10
BVSO	4-vinylpyridine	0.03	6.24	10
BVSO	2-methyl-5-vinylpyridine	0.02	5.61	10
BVSO	3-vinylpyridine	0.02	7.82	10
BVSO	acrylonitrile	0.28	3.0	10
BVSO	acrylamide	0.28	3.31	10
BVSO	methacrylic acid	0.32	2.51	10
OVSO	styrene	0.02	7.00	10
OVSO	methyl methacrylate	0.04	10.2	10
OVSO	acrylonitrile	0.24	3.0	10
OVSO	acrylamide	0.25	3.2	10
p-tolyl VSO	styrene	0.1	5.77	11

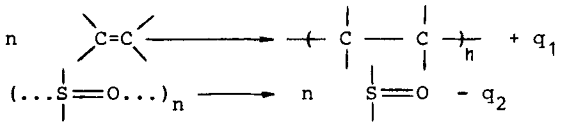
Copolymerizations of alkyl vinyl sulfoxides with vinyl monomers proceed at low rates and the content of sulfoxide groups in the resulting copolymer is rather low compared to the composition of the monomer mixture. Only in copolymerizations of MVSO and EVSO with vinyl acetate the sulfoxide monomer is of higher activity than the latter.[7] An increase in the content of vinyl sulfoxide in the monomer mixture and, consequently, in the copolymer so obtained results in a decreased molecular weight of the copolymer.[10]

The size of an alkyl substituent in a vinyl sulfoxide influences in fact neither the copolymerization rate nor the monomer's involvement in copolymerizations.

Increasing size of the alkyl substituent leads to changes in some physical characteristics of the copolymer. Thus, poly-(BVSO-co-acrylamide) containing up to 50 mole-% of sulfoxide groups is water soluble, while poly-(octyl vinyl sulfoxide-co-acrylamide) fails to dissolve in water when the content of octyl vinyl sulfoxide (OVSO) groups reaches approximately 40 mole-%.[13]

The heat of BVSO copolymerization with vinyl monomers depends essentially on the temperature: a slight temperature increase results in an increased effective heat of copolymerization.[14] The observed dependence is modified by two competing processes, *i.e.* of an exothermic and endothermic one corresponding to the copolymerization and decomposition of vinyl sulfoxide associates, respectively,

SCHEME 1



A certain portion of the heat liberated in the copolymerization is consumed by the decomposition of vinyl sulfoxide associates (the regeneration of the associative bonding in the copolymer being impeded) which leads to the lower heat of copolymerization observed. At higher temperatures the concentration of the sulfoxide associates becomes lower and, besides, the number of associates decreases because they decompose and absorb the heat of copolymerization, a process which is responsible for increased liberation of heat with increasing temperature.

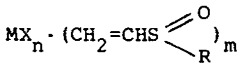
The incorporation of the vinyl sulfoxide into the coplymer is determined by the type of the vinyl copolymer. Vinyl sulfoxides exhibit their highest reactivity in copolymerizations with vinyl monomers capable of forming complexes with them (acrylamide, methacrylic acid, acrylonitrile).[10]

The vinyl sulfoxide activity is also strongly affected by the solvent,[5,10,15] becoming higher as one changes from electron-donor to proton-donor solvents. The complex formation between the vinyl sulfoxide and the solvent (as well as between the vinyl sulfoxide and acrylamide, methacrylic acid, and acrylonitrile as comonomers) leads to a change of electron density in the vinyl sulfoxide molecule with concomitant blocking of the $>S=O$ group and results in increased reactivity of the vinyl sulfoxide and lowers its activity in chain transfer reactions. Besides, the stronger the complex formed the higher is the activity of the $>C=C<$ bonds in copolymerizations.

One could anticipate that the employment of stronger complexing agents should further activate vinyl sulfoxides in copolymerizations. Indeed, the authors of Ref. 5 reported that addition of $ZnCl_2$ and $SnCl_4$, respectively, to the EVSO-styrene system, the additives forming strong complexes with $>S=O$ groups, leads to increasing effective constants of vinyl sulfoxide copolymerizations. Thus, copolymerization of EVSO with styrene gives $r_1 = 0.01$ and $r_2 = 7.0$, whereas in the presence of 0.3 mole of $ZnCl_2$ per mole of EVSO in benzene solution the copolymerization constants assume the values $r_1 = 0.05$ and $r_2 = 2.0$, the copolymer becoming enriched in sulfoxide groups.

In the reports given in Refs.[6,10,14,16,17] copolymerizations of vinyl monomers, *i.e.* of styrene, acrylonitrile, methyl methacrylate, and vinyl acetate, with alkyl vinyl sulfoxide complexes of 3d-metal chlorides and nitrates, are described.

SCHEME 2



$MX_n \cdot (CH_2{=}CHS(O)R)_m$

M = Co(II), Zn(II), Mn(II), Cu(II), Fe(III), Cr(III);

X = Cl, NO_3; R = C_4H_9, C_8H_{17};

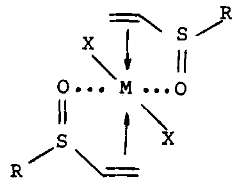
n = 2,3; m = 2–4

The introduction of vinyl sulfoxides as their complexes with 3d-metal salts into copolymerization results in a higher concentration of sulfoxide groups in the copolymers, the copolymerization rate and the copolymers' molecular weights increasing at the same time.

This increase in the activity of vinyl sulfoxides takes place in all the alkyl vinyl sulfoxide complex-vinyl monomer systems studied with the exception of the cases where copper salts and ferric chloride are used as complexing agents, in the presence of which no copolymerization occurs. This is obviously caused by the strong inhibitory effect of copper and iron halides and their sulfoxide complexes on these radical processes.[18]

The reactivity of alkyl vinyl sulfoxides in copolymerizations is increased as a consequence of complex formation. The IR spectra of vinyl sulfoxide complexes of metal salts show that the valency vibration band of the complexed >S=O group is shifted towards the low-frequency region by 50–90 cm^{-1} as compared to the free sulfoxide group which shows that the metal ion is coordinated to the sulfoxide group oxygen. Spectrophotometric studies of alkyl vinyl sulfoxide complexes $MX_n \cdot($ $SOR)_m$[17] prove that the metal ion is coordinated by the sulfoxide group oxygen with direct interactions between the vinyl sulfoxide double bond π-electrons and the vacant d-orbitals of the metal atom:

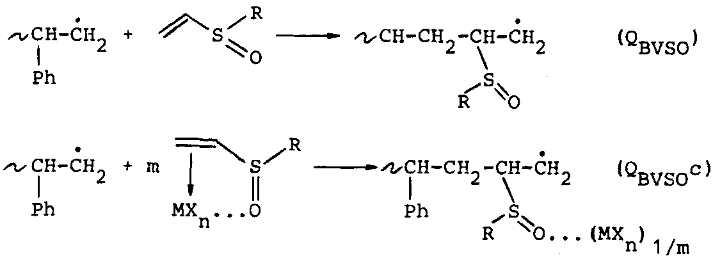
SCHEME 3



Thus, the IR spectra of the complexes show that the valency vibration band of the >C=C< bond is broadened and shifted from 1600 to 1610–1640 cm^{-1}; in the ^{1}H NMR spectra the signals of the double bond protons are shifted 1 ppm to lower field; the ^{13}C NMR spectra demonstrate that the electron density at the α- and β-carbon atoms of the vinyl group has been equalized.

The interactions of the multiple bonds with metal atoms result in a three- to four-fold increase of the reactivity of vinyl sulfoxide complexes of 3d-metal salts in radical additions across the double bond (additions of polystyrene radicals have been investigated) compared to that of uncomplexed vinyl sulfoxides.

SCHEME 4



COMPLEX	$MnCl_2\cdot2$ BVSO	$CoCl_2\cdot2$ BVSO	$CrCl_3\cdot3$ BVSO	$ZnCl_2\cdot2$ BVSO
Q_{BVSO^c}/Q_{BVSO}	3.2	3.4	3.8	4.4

BVSO complexes of iron and chromium nitrates such as $Fe(NO_3)_3\cdot3$ BVSO and $Cr(NO_3)_3\cdot3$ BVSO isolated from solutions, stored, and heated decompose[10] to give oxides of nitrogen, sulfur, metal, and coke-like products. The process is of self-accelerating and explosive character with an induction period depending on temperature, medium viscosity, complex composition, and metal type. This is evidently caused by the spontaneous polymerization of the spatially organized monomer intermediates formed. The high exothermicity of the polymerization results in the decomposition of the complex.

As follows from a comparison of the results reported[5,10], maximum activity of vinyl sulfoxides in radical polymerization is observed after complete coordination of the sulfoxide group to the complexing agent (Table 3).

Table 3. Parameters of styrene (M_2) copolymerization with alkyl vinyl sulfoxides and their complexes (M_1)* **

M_1	r_1	r_2	Q_1	Ref.
EVSO	0.02	7.0	0.05	5
BVSO	0.02	7.21	0.05	10
$ZnCl_2\cdot3$ EVSO	0.05	2.0	0.14	5
$ZnCl_2\cdot2$ BVSO	0.21	2.31	0.22	10

The vinyl sulfoxide activity is affected by the extent of the $>S{=}O$ group involvement in the coordination sphere of a complexing agent.[16] Thus, the copolymerization of vinyl sulfoxide complexes of the nitrates of cobalt, manganese, and zinc with vinyl monomers has shown that the reactivity of the complexes $M(NO_3)_2\cdot2$⌃SOR is higher than that of the complexes $M(NO_3)_2\cdot4$⌃SOR (Table 4).

---

* R_2SO and $ZnCl_2$ for complexes of the composition $ZnCl_2\cdot2\ R_2SO$

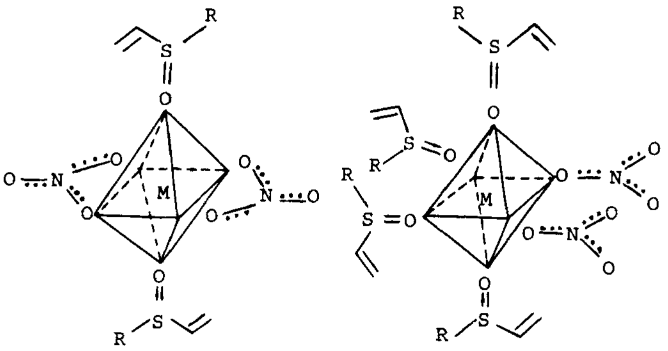
** As shown earlier, the copolymerization constants of alkyl vinyl sulfoxides of different alkyl size are practically the same

Table 4. Parameters of acrylonitrile (M_2) copolymerization with OVSO and its complexes $Co(NO_3)_2$.n OVSO (M_1)

M_1	r_1	r_2	Q_1
OVSO	0.24	3.0	0.1
$Co(NO_3)_2 \cdot 4$ OVSO	0.38	2.4	0.17
$Co(NO_3)_2 \cdot 2$ OVSO	0.53	1.8	0.27

The difference in the activity of the above complexes is modified by the varying positions of the vinyl sulfoxide molecules in the complex coordination spheres due to the ability of the nitrate ion to act as both mono- and bidentate ligand:

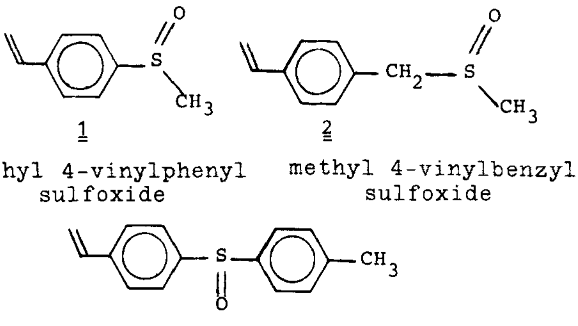
SCHEME 5



Vinyl sulfoxides subjected to copolymerization as their complexes with 3d-metal salts afford copolymers with a sufficiently high reaction rate, the copolymers formed being enriched with complexed sulfoxide groups. The subsequent decomposition of the polymer complex results in polysulfoxides with a content of S=O groups up to 80 mole-%, much higher than in the copolymerization of uncomplexed vinyl sulfoxides.

Styrene derivatives containing a sulfoxide moiety (1–3)[19,20] are readily homopolymerized and copolymerized with vinyl monomers under radical conditions (Table 5).

SCHEME 6



1
methyl 4-vinylphenyl
sulfoxide

2
methyl 4-vinylbenzyl
sulfoxide

3
p-tolyl 4-vinylphenyl
sulfoxide

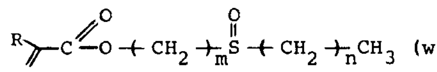
Table 5. Parameters of **1** and **2** (M_1) copolymerization with styrene (M_2)[19]

M_1	M_2	r_1	r_2	Q	$\bar{e}$
1	styrene	0.56	0.26	1.19	0.58
2	styrene	0.52	0.60	1.03	0.28
	styrene			1.0	−0.80

Compounds **1** and **2** turn out to be more active monomers than styrene. This result conforms with corresponding data on styrene derivatives with electron-acceptor groups which polymerize more readily than styrene itself.

Radical polymerization of **3** leads to the formation of optically active poly-[*p*-(*p*-tolylsulfinyl)styrenes with an osmometric molecular weight of approximately $3–15 \cdot 10^3$. Its oxidation with H_2O_2 gives the corresponding optically inactive polysulfone.[20]

SCHEME 7


(with R = H, CH_3; m = 2-4; n = 0, 1)

Alkylsulfinyl(meth)acrylates (Scheme 7) homopolymerize[21,22] in the presence of radical initiators to give water-soluble polymers. Moreover, they copolymerize easily with vinyl monomers containing steroid or alkaloid moieties at the double bond.[21,22] The polymers thus formed possess physiologic activity.

For the first time, the homopolymerization of alkyl vinyl sulfoxides by an ionic mechanism[25] succeeded in the presence of organometallic catalysts, *i.e.* of a sodium naphthalene adduct, butyllithium, and naphthylsodium. The process proceeds at a high rate to form oligomers.

An optically active polymer has been prepared with *p*-tolyl vinyl sulfoxide in THF in the presence of *n*-BuMgBr.[26] Its reduction with $LiAlH_4$ and oxidation with H_2O_2 gave optically inactive polysulfide and polysulfone, respectively.

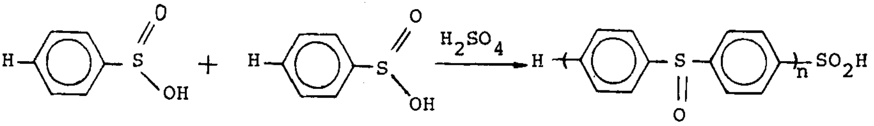
Under similar conditions, *m*-tolyl vinyl sulfoxide also forms an optically active polysulfoxide[27] with $[\alpha]_D = 270°$ and a molecular weight of 3500. Its optical activity can be increased by polymerization in the presence of (−)-sparteine which gives a polymer with the optical activity $[\alpha]_D = 310°$. However, the oxidation of poly-(*m*-tolyl vinyl sulfoxide) with H_2O_2 results in a decrease of its optical activity to $[\alpha]_D = 19–40°$. The residual activity is probably due to incomplete oxidation of the sulfoxide groups.

In the presence of organometallic compounds, optically active vinyl phenyl sulfoxide gives dimers[28,29] and polymers.[30]

Polysulfoxides containing $>S=O$ groups in the backbone are usually obtained by polycondensation and addition polymerization.

The first communication on polysulfoxides synthesized by polycondensation dates as far back as 1910. With an arylsulfinic acid dissolved in concentrated H_2SO_4, Hilditch[31] observed the formation of insoluble and alcohol-swelling products, the latter later identified as poly (phenylene sulfoxides):[32]

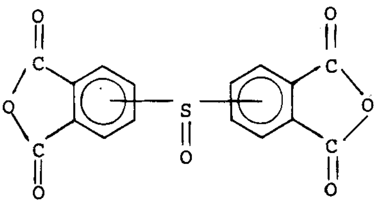
SCHEME 8



The reaction of phosgene with bis-(4-hydroxyphenyl) sulfoxide affords a polycarbonate with sulfoxide groups (m.p. 230–250 °C).[33] A polycarbonate based on bis-(4-hydroxy-3-methylphenyl) sulfoxide melts at 190 °C.[34] Thermo-, light-, and chemostable poly(sulfoxide-co-carbonates) resistant to cracking have been prepared by interaction of 4,4′-dihydroxydiphenyl, 4,4′-dihydroxy-3,3′-dichlorodiphenyl, 4,4′-dihydroxy-3,3′,5,5′-tetrachlorodiphenyl sulfoxide and compounds possessing *N*,*N*′-carbonyl groups.[35]

On the basis of a copolymer of bis-(3,4-dicarboxyphenyl) sulfoxide dianhydride with bis-(4-aminophenyl) ether[36] (Scheme 9), polymer films of high chemical stability (glass temperature 324 °C) have been produced.

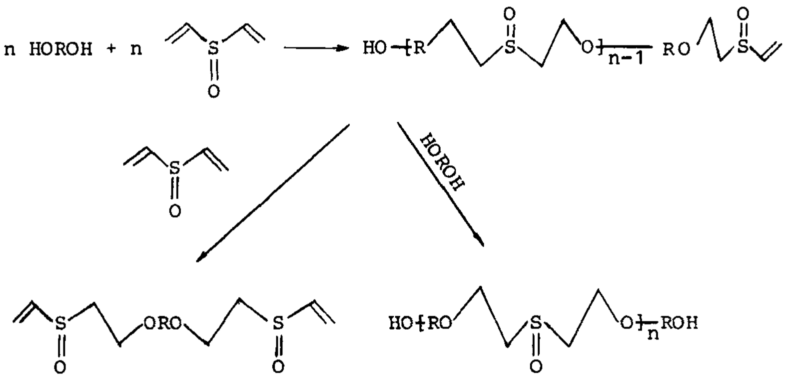
SCHEME 9



Michael addition polymerization[37] of glycols, diamines, and dithiols with divinyl sulfoxide (DVSO) represents a convenient route to polysulfoxides containing various functional groups.

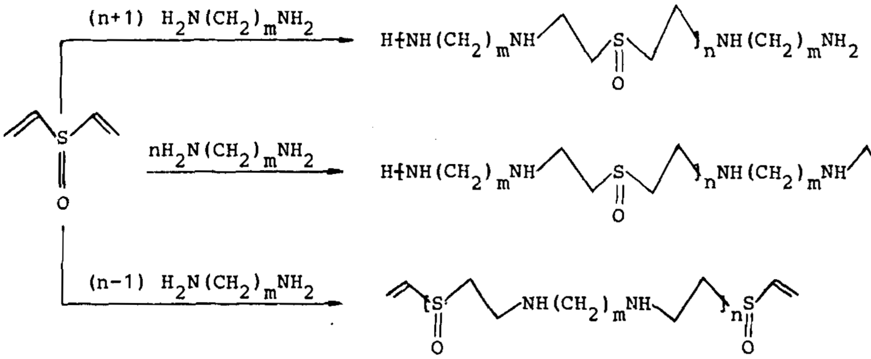
The addition polymerization of glycols with DVSO[38,39] afforded oligosulfoxides of molecular weight 500–1500 in quantitative yields:

SCHEME 10



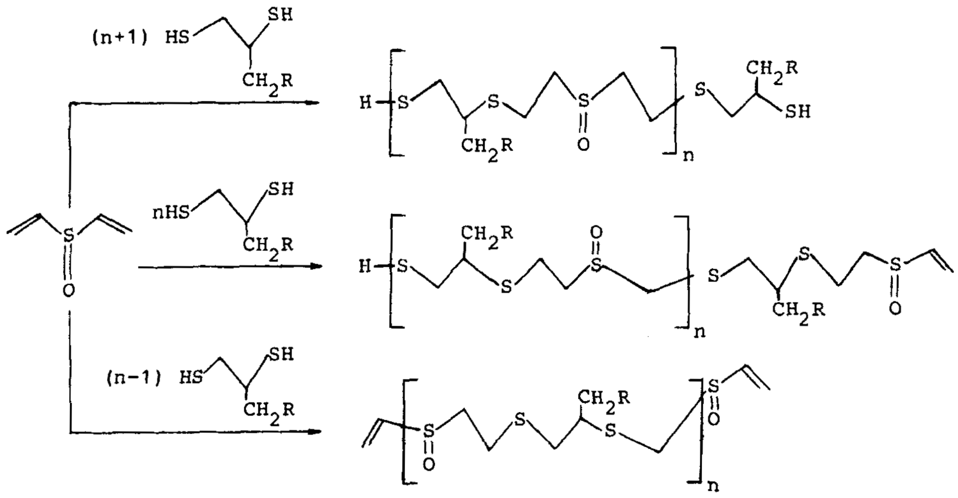
By addition polymerization of diamines with DVSO[40,41] polymers have been synthesized which contain alternating >SO and NH groups in the main chain and reactive $CH_2=CH$- and NH_2- end groups:

SCHEME 11



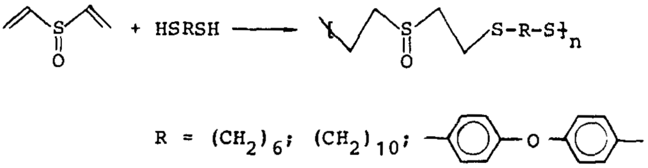
Nucleophilic addition polymerizations of dithiols with DVSO[42,43] afford oligo(ethylene sulfoxides) (MW 1100–1300) with a content of active vinyl or mercapto end groups:

SCHEME 12



Poly-[alkylene(arylene)thioalkylene sulfoxides] have been obtained analogously:[44]

SCHEME 13



Thus, addition polymerization and polycondensation afford a number of polysulfoxides characterized by sulfoxide groups positioned either in the side or the main macromolecule chain, by the "specific weight" of the > S=O moiety in the total polymer bulk, and by the presence of various other functional groups.

Polymer Modifications

Polymer modifications make it possible to introduce an > S=O group into both the main and the side chains of macromolecules. Most frequently, polysulfide oxidations have been carried out to synthesize polymers with sulfoxide groups.

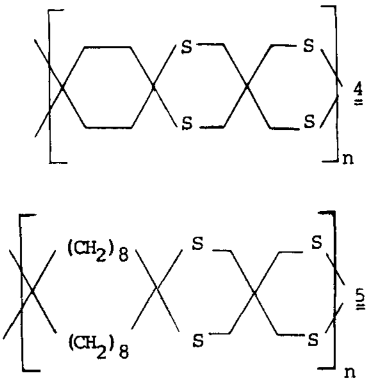
Various oxidizing agents have been employed to carry out these oxidations. Poly-(phenylene sulfoxides) of high thermal stability have been synthesized from poly(phenylene sulfides) by oxidation with concentrated nitric acid. By oxidation of poly-(*p*-phenyleneoxyphenyl sulfide) with 30% H_2O_2 in acetic acid in the presence of H_2SO_4, a polymer containing sulfide, sulfoxide, and sulfone groups in the ratio 47:23:20 is obtained.[47,48] The same authors also investigated the oxidation of poly-(oxy-di-*p*-phenylene sulfide) which, when oxidized with di-*t*-butyl peroxide or H_2O_2 in halohydrocarbons affords copolymers possessing, depending upon the conditions employed, either sulfide and sulfoxide or sulfoxide and sulfone blocks.[49]

Aliphatic polysulfides upon oxidation with hydrogen peroxide give the corresponding polysulfoxides.[50-56]

Oligomers possessing alkyl sulfoxide end groups have been prepared by polymerization of a vinyl monomer in the presence of a thiol and further oxidation with hydrogen peroxide.[57]

Oxidation of polysulfides **4** and **5** leads to the corresponding sulfoxide-containing spiro polymers.[58]

SCHEME 14



4

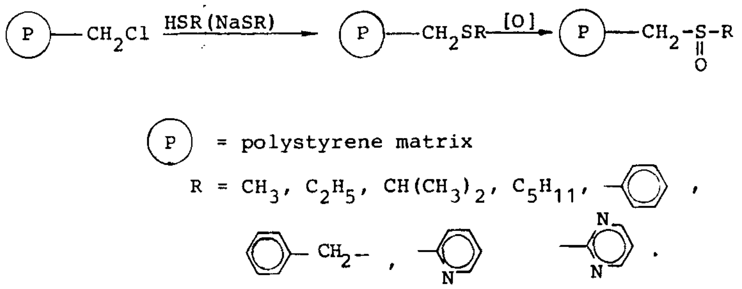
5

Polysulfoxides possessing nitrogen atoms in the main chain have been prepared[60,61] by oxidation of a polyamide containing $NHCO(CH_2)_2S(CH_2)_3$ groups[59] with hydrogen peroxide and by the corresponding oxidation of the reaction products of epoxides with $CS(NH_2)_2$ or NH_4SCN (also Na_2O_2 and $Na_2S_2O_8$ have been used as oxidants). A method to synthesize polysulfoxides by selective oxidation of 1,2,4-thiodiazole-2,5-dithiol has been suggested.[62] The oxidation was conducted in the presence of transition metal ions with either a 30% solution of H_2O_2 in acetic acid or molecular oxygen activated by UV or visible light.

A number of reports describe the production of polysulfoxides by transformations of chloromethylated polystyrene. The chloromethyl group can be converted to a sulfoxide-containing function in different ways:

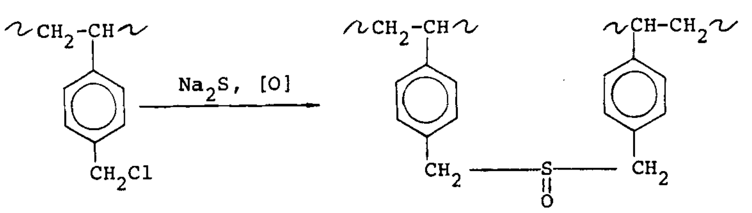
a) via a sulfide group which is further oxidized[63-67]

SCHEME 15



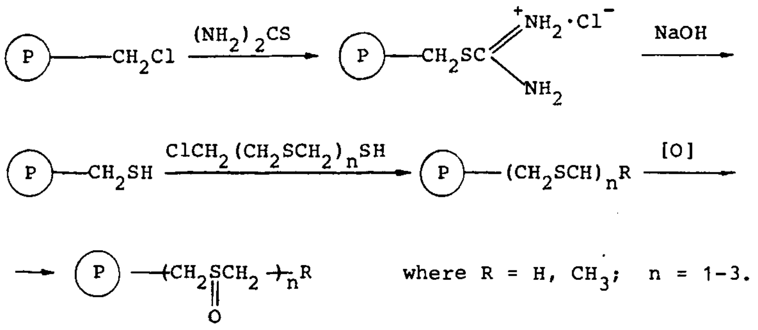
The following reagents for selective oxidation of sulfides to sulfoxides are used as oxidizing agents: *N*-chlorosuccinimide/MeOH; HNO_3/Ac_2O; H_2O_2-*t*-BuOH/V_2O_5. With sodium sulfide a cross-linked polystyrene reticulated by inter- and intramolecular sulfide bridges is formed the oxidation of which leads to the corresponding sulfoxide.[68]

SCHEME 16



b) the CH_2Cl group can be transformed to a group containing up to three sulfoxide units according to the scheme below[68,69]

SCHEME 17



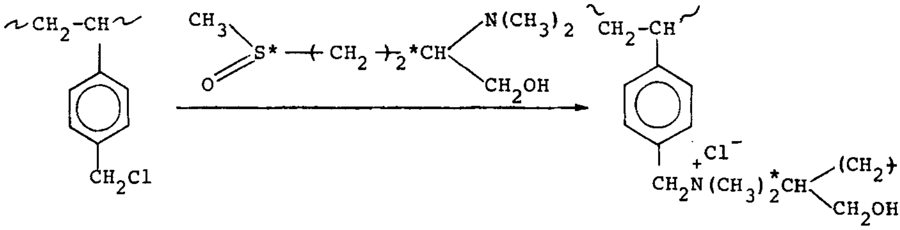
A cross-linked poly-(methyl *p*-vinylphenyl sulfoxide) was prepared by interaction of poly-(methyl *p*-vinylphenyl sulfide) with dimethyl sulfate; the resulting sulfonio polymer was subsequently transformed to a sulfoxide polymer by treatment with a DMSO-benzaldehyde mixture in the presence of potassium *t*-butoxide.[70]

Poly-(vinyl sulfides) and poly-(*t*-butyl vinyl sulfide) and their copolymers with methyl methacrylate and styrene have been oxidized with optically active percamphoric acid[71] to afford optically active polysulfoxides, which may also result from biooxidation of poly-(vinyl sulfides) and their copolymers with maleic anhydride by *Aspergillus niger* and *Penicillum notatum*.

Polymer membranes with high permeability for polar molecules have been prepared by oxidation of the methionine unit in a copolymer of *d,l*-methionine-*N*-carboxy anhydride with *d,l*-leucine *N*-carboxy anhydride.[72]

Polymers containing methionine sulfoxide units have been also made by grafting preoxidized modified methionine on a polymer matrix:[73]

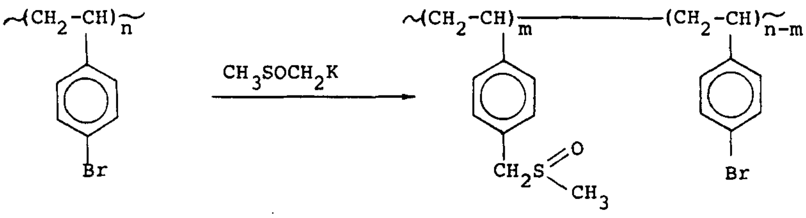
SCHEME 18



In thiol-polybutadiene adducts oxidized to the corresponding polysulfoxides with hydrogen peroxide[74] sulfide and sulfone groups were always observed in addition to the end product's sulfoxide groups, one explanation being the different solubilities of the pre- and post-oxidation polymer. However, according to[75] all attempts to carry out a selective oxidation of the poly-sulfides failed despite the fact that the medium could be kept homogeneous throughout the reaction. Also the oxidation of low-molecular sulfides with selective oxidants led to a mixture of products. In the oxidation of high-molecular poly-sulfides steric hindrance appears to block the approach of the oxidant to the more "inaccessible" sulfide groups while the more "accessible" ones are readily oxidized to sulfoxide groups and beyond that to sulfone groups.[75]

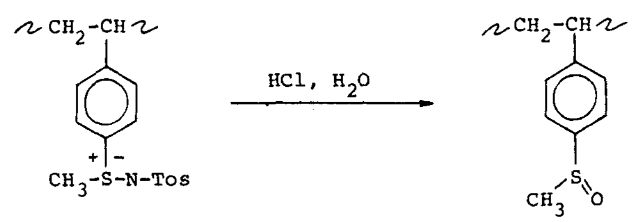
Also, polymers containing alkyl phenyl (benzyl) sulfoxide groups have been prepared by treatment of brominated polystyrene with potassium methylsulfinylmethanide[64] and

SCHEME 19



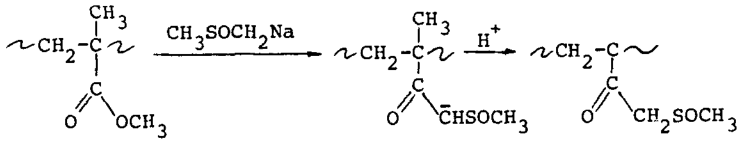
by hydrolysis of poly(phenyl vinyl sulfilimine):[76]

SCHEME 20



It should be noted that in the first case there took place an incomplete substitution of bromine, whereas the hydrolysis of the sulfilimine group was quantitative. Poly(keto sulfoxides) have been prepared by interaction of polymers containing ester groups with sodium methylsulfinyl-methanide and subsequent acid treatment of the primary product.[77,78] Poly-(methyl methacrylate) and poly-(methyl methyacrylate-co-styrenes) were used as the polymers carrying the ester groups. The poly-(keto sulfoxides) formed contained mostly *β*-keto sulfoxide side chains and, besides, *β*,*β*′,-diketo sulfoxide side chains ($\begin{smallmatrix}-\mathrm{CO}\\-\mathrm{CO}\end{smallmatrix}$ $\mathrm{CHSOCH_3}$).

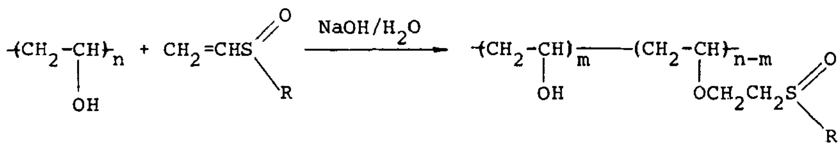
SCHEME 21



The formation of diketo sulfoxide side chains is due to the interaction of an α-keto α-sulfinylmethanide anion with an adjacent ester group. The reaction of $\mathrm{CH_3SOCH_2Na}$ with a copolymer without methyl methacrylate chain blocks (28 mole-%) yielded a product where the copolymer ester groups were completely transformed to *β*-keto sulfoxide groups only.

Subjection of poly-(vinyl alcohol) and alkyl vinyl sulfoxides to the Michael reaction[79] affords copolymers with sulfoxide side chains.

SCHEME 22



Therefore, polymer modifications are considered to be well-suited to produce polysulfoxides of various structures. It should be noted, however, that no success can usually be expected for attempts to complete a series of transformations by generating the sulfoxide groups in the last step.

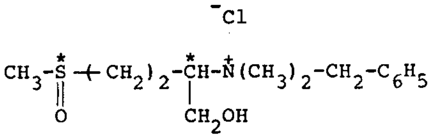
PROPERTIES AND APPLICATIONS OF POLYMERS CONTAINING SULFOXIDE GROUPS

Taking into account the existence of only a limited number of reports concerning polysulfoxides one can conclude that polymeric sulfoxides possess both the properties characteristic of their low-molecular analogs and also novel due to the fact that the S=O groups are embedded in a polymer chain, *i.e.* by the polymer state of the compound in question.

Most of these reports are concerned with studies of polysulfoxides' catalytic activity in phase transfer catalysis.[65,68,73,80-84]

Among the first publications revealing the potential of sulfoxide side chain-containing polymers as phase transfer catalysts one[73] describes investigations of the catalytic activity of cross-linked polystyrene with a content of chiral methionine derivatives in Michael additions of nitromethane to *trans*-chalcone, thiophenol to 2-cyclohexen-1-one, and of methyl vinyl ketone to the methyl ester of 1-oxoindane-2-carboxylic acid. The polysulfoxide activity appeared comparable to and higher than that of the soluble analog.

SCHEME 23

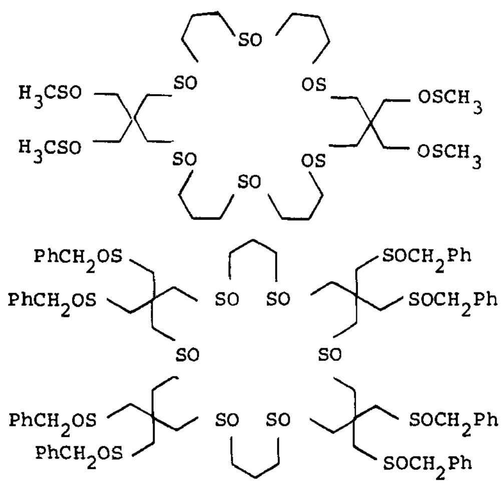


$$\underset{\underset{O}{\|}}{CH_3-\overset{*}{S}}\!+\!CH_2)_2-\underset{\underset{CH_2OH}{|}}{\overset{*}{C}H}-\overset{\overset{{}^{-}Cl}{+}}{N}(CH_3)_2-CH_2-C_6H_5$$

The most detailed studies of polysulfoxides were carried out with nucleophilic substitution in alkyl halides.[65,68,80-83] With respect to polysulfoxide type, *i.e.* either linear (soluble) or cross-linked (insoluble), the reactions were conducted under the conditions of phase transfer catalysis in a biphasic liquid-liquid, or in a triphasic liquid-solid-liquid or solid-liquid-solid system. In all cases the polysulfoxides were catalytically active, whereas with low-molecular sulfoxides (DMSO, phenyl methyl sulfoxide, and benzyl methyl sulfoxide) as catalysts halogen substitution by nucleophiles did not occur. Polymeric sulfoxides are also important owing to their regenerating ability. Thus, in most cases their activity remains unchanged after regeneration.

The macrocyclic crown sulfoxides described in[84-86] exhibit high catalytic activity in the phase transfer monoalkylation of $PhCH_2CN$ and $PhCH_2COCH_3$ with alkyl halides, their activity being higher than that of acyclic sulfoxides.

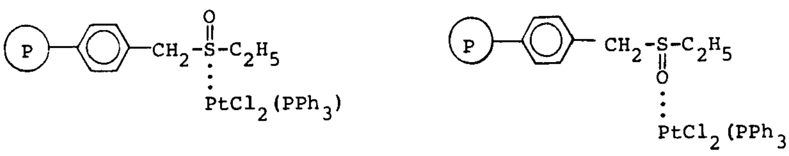
SCHEME 24



Polysulfoxides have been employed as polymeric DMSO analogs in oxidations.[64,66] Their oxidative ability was slightly different from that of low-molecular sulfoxides. Thus, when benzyl chloride was oxidized to benzaldehyde the reaction yielded 84% in the presence of DMSO, 56% in the presence of benzyl ethyl sulfoxide, and 54% with the use of a polymeric sulfoxide such as Ⓟ-$CH_2SOC_2H_5$.[64]

The same polysulfoxides can give polymeric complexes with platinum compounds, which can be applied to catalytic organic synthesis. It should be noted here that the sulfoxide groups coordinate at both sulfur and oxygen.[64]

SCHEME 25



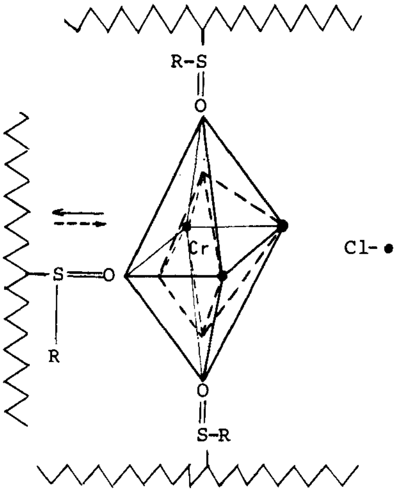
The use of sulfoxide-containing polymers to meet the requirements of medicine represents a promising trend. Water-soluble copolymers based on sulfoxide-containing monomers[23,24] afford polymeric steroid and alkaloid derivatives of increased biologic activity. Biological tests prove copolymers with a morphine antagonist joined to them to act much longer and to be less toxic[24] as compared to the "free" form. Membranes based on polysulfoxides[22,72] with appropriate permeability for drugs can be usefully applied for biomedical purposes.

In recent years, some reports concerning various aspects of the application of modified alkyl vinyl sulfoxides of poly(vinyl alcohol) (PVA) have been published.[79,87-91] Special attention has been given to the penetration of sulfur dioxide through polymeric membranes obtained on the basis of the compounds cited above.[87,88] While PVA exhibits rather low penetrability coefficients, its copolymer containing sulfoxide groups gives higher K_p values and, besides, high separation factors for mixtures such as SO_2/N_2 and SO_2/CO_2 ($P_{SO_2}/P_{N_2} = 2 \cdot 10^4$; $P_{SO_2}/P_{CO_2} = 3 \cdot 10^4$).

Sulfoxide-containing polymers can be used as selectively permeable membranes for the isolation of SO_2 as well as as effective adsorbents for sulfur dioxide.[92,93] Thus polysulfoxides based on poly-(alkyl vinyl sulfoxide-co-acryl amide) and (-co-4-vinylpyridine) possess high adsorption capacity (up to 900 mg SO_2/g polymer) and are easily regenerated. They are completely released from the sulfur dioxide sorbate at 60–90 °C and under weak vacuum ($1.33 \cdot 10^4$ Pa). Multiple sorption-desorption cycles give no decrease in their adsorption characteristics. Poly(4-vinylpyridine-co-alkyl vinyl sulfoxides) and modified PVA may become important for isolating SO_2 from combustion and flue gases.

Of peculiar interest are the properties of d-metal polysulfoxide complexes. Thus, organic glasses based on copolymers of methyl methacrylate with chromium chloride-alkyl vinyl sulfoxide complexes ($CrCl_3 \cdot 3\,CH_2{=}CHSOR$) can undergo reversible thermochromic transformations.[94] The color of the copolymers changes from emerald green (at the temperature of liquid nitrogen) to violet (at 40–50 °C). Thermochromic transformations occur due to changes in the configuration of the polymer complex coordination sphere as a consequence of the changed mobility of the polymer matrix, the scheme below demonstrating the case.

SCHEME 26



Upon lowering of the temperature the matrix' rigidity increases with distortion of the complex configuration; as the temperature increases the activity of the polymer chains increases and the octahedron resumes its initial shape. The effect of the polymer matrix on the polymer complex configuration is proven by the fact that poly(methyl methacrylate) filled with chromium dialkyl sulfoxide complexes not chemically joined to the macromolecule possesses no thermochromic properties.

Polymer complexes of $MoCl_3$ and polysulfoxide SO groups obtained by both the polymerization of methyl 4-vinylphenyl or 4-vinylbenzyl sulfoxides and the oxidation of polysulfides can act as redox initiating systems.[95-99] After the oxidation of $MoCl_3$ by the polysulfoxide there are formed R-S-R radicals initiating the vinyl polymerization. The employment of this initiating systems affords various graft copolymers with desirable properties.

Particularly attractive are data[100] on compounds prepared to register information, based on the ability of an $>$ SO group to form complexes with transition metal salts. The method consists in the exposition of a photosensitive halogen-silver layer and the treatment thereof in the presence of a compound containing optically active poly(*p*-tolyl vinyl sulfoxide) with a $TiCl_3$ developing solution. In the sections exposed part of the $TiCl_3$ is consumed for the development and the unconsumed part diffuses into the sulfoxide-containing layer to react with the polysulfoxide, thus destroying the chirality. The image appears in the sulfoxide-containing layer seen with polarized light.

Polysulfoxides prepared by both the polycondensation of bifunctional sulfoxide-containing monomers[33-36] and the oxidation of sulfur bridges in poly(phenylene sulfides)[45,46] possess high thermo- and chemostability and are thus useful for the production of fibers, films, thermoresistant adhesives, and molding materials of high thermostability. Additional treatment of poly(phenylene sulfoxide) in argon at 350–700 °C affords polymers with decomposition temperatures above 600 °C.[101] The halogenation of a linear poly(phenylene sulfoxide) with chlorine, bromine or iodine and the subsequent thermal treatment with sulfides of alkali, alkali-earth, and transition metals results in cross-linked polymers of high adhesion to metal, glass, and wood.[102]

In addition to these potential uses of polysulfoxides there exist a great number of additional communications, mostly as patents, considering various uses of polymers containing sulfoxide groups in both the main and the side chain. Thus, polysulfoxides can be used as physiologically active compounds,[25,56,62,75] adhesives[25,103] and detergents[51,104] as well as to remove petroleum and oil from sewage water[60,61] and to prepare cosmetic compositions.[105-108]

In conclusion it can be said that the sulfoxide properties reveal themselves most effectively with the SO group positioned in the side chain. Quite evidently, there would have appeared much more information on the properties of polysulfoxides if more effective methods for their synthesis were known, appropriate to produce polymeric molecules with a high content of sulfoxide groups.

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