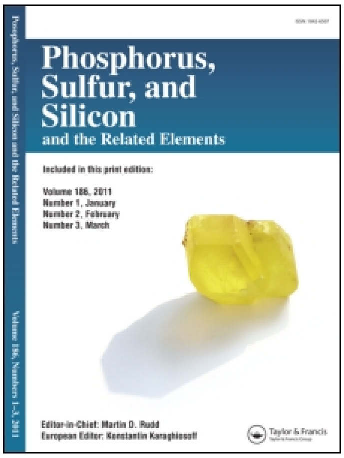

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Polymers Containing Sulfur in the Main Chain Synthesis, Properties, Applications

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To cite this Article Spassky, Nicolas(1993) 'Polymers Containing Sulfur in the Main Chain Synthesis, Properties, Applications', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 71 — 92
To link to this Article: DOI: 10.1080/10426509308038102
URL: http://dx.doi.org/10.1080/10426509308038102

Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 71–92
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POLYMERS CONTAINING SULFUR IN THE MAIN CHAIN SYNTHESIS, PROPERTIES, APPLICATIONS

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Abstract

A description is given of the most representative polymers containing sulfur atom in the main chain. The general ways of synthesis of such polymers are described. The stereochemical aspects of ring-opening polymerization of cyclic sulfides are discussed and the variations of physical properties in function of enantiomeric composition are examined.

INTRODUCTION

Sulfur-containing polymers are very numerous and many examples of them were studied. Sulfur atoms may be included in the main chain or be present in the side chain, for instance like in polythiols or in polypeptides with S-containing amino acids. In this brief review, we shall examine only polymers containing S atoms in the main chain and for which S atom is involved directly in the synthesis of these materials.

As a general trend -S- bridges introduce flexibility in the chain, while a functional group like -SO_2- increase stiffness and stability to oxidation. Thus the properties of polymers and their potential applications may be guided by such considerations.

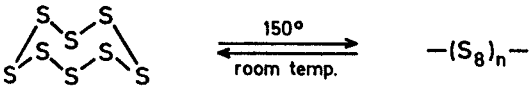
Few general reviews covering all families of S-containing polymers are available[1-3]. Much more of them exist on particular families of sulfur polymers. They will be indicated along the text.

After a condensed description of the most important and representative members of sulfur containing polymers, a chapter will be devoted to the main general methods of synthesis of the latter. Few individual examples of preparations are given. For more details, it is recommended to consult the general reviews cited above. At last, some particular stereochemical aspects related to the ring-opening polymerization of cyclic sulfides will be discussed and the differences in physical properties of polymers prepared by this method examined in function of their enantiomeric composition.

DIFFERENT TYPES OF S-CONTAINING POLYMERS

POLYMERIC ELEMENTAL SULFUR

This is simplest sulfur-containing polymer. The elemental sulfur is found under a stable eight-membered ring form and on heating above 150°C an equilibrium mixture of polymeric linear chains and cyclo octasulfur is formed :



The chemistry of polymerization of sulfur has been extensively reviewed[2,4] as well as its copolymers with different comonomers[2,5-7].

POLY(MONOSULFIDE)S

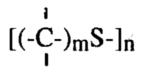
Poly(monosulfide)s form a very large group of polymers containing a monosulfide linkage in the main chain and corresponding to the general formula :

$$(\text{-R - S-})_n$$

Depending on the nature of -R-, different important families of polymers may be distinguished.

Aliphatic poly(monosulfides) or polythioethers

These polymers having the general formula :



$$[(\text{-}\overset{|}{\underset{|}{C}}\text{-})_m S\text{-}]_n$$

may be prepared by ring-opening polymerization, polycondensation or polyaddition methods[1,2,3,8]. Attempts to develop industrial applicability for poly(monosulfides) have been made in years sixties particularly by ring-opening polymerization and copolymerization of thiiranes. Poly(ethylene sulfide) ($-CH_2CH_2S-$) is a crystalline plastic with some properties better than polyformaldehyde and copolymers of propylene sulfide ($-CH(CH_3)CH_2S-$) are good elastomers with solvent resistance. These polymers are however oxydable and the price of monomers is still elevated.

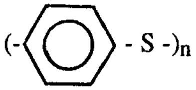
These is also a theoretical interest in the polymerization of thiiranes, particularly substituted one, which may give stereoregular polymers. They will be discussed later.

Poly(thietane)s (m = 3) has been particularly studied from the point of view of mechanism and kinetics of cationic polymerization[9].

Poly(thioacetal)s (m = 1) were less extensively studied than the corresponding polyacetals mainly because of the instability of thiopolymers in the molten state. Halogeno and particularly fluoro derivatives were homopolymerized and copolymerized with different vinyl and diene derivatives[10,11].

Aromatic polymonosulfides or poly(arylene sulfide)s

In this class of polymers, where R is an aromatic moiety, the most important product is poly(phenylene sulfide) (PPS)



a commercial plastic produced by Philips Petroleum under the trade name of Ryton[12] having an excellent set of properties. This polymer is highly crystalline (m.p. ~ 285°C), insoluble in most of the solvents at room temperature, but can be solubilized in high-boiling solvents at elevated temperatures.

The process of preparation developed by Edmonds and Hill involves the reaction of p-dichlorobenzene with sodium sulfide in a polar solvent at high temperature[12]. Many other procedures of synthesis are available but are not commercially applied[13,14] PPS possesses unusual chemical resistance, good mechanical properties, high thermal stability. A great variety of injection-molding compounds are available containing glass reinforcement, mineral fillers, pigments, different additives, etc...[15] PPS finds electrical, electronic, mechanical applications. It is used in coatings, as composite[16] material and in thermoplastic prepregs. Although in many applications it is used as electrical insulator, it can be rendered electrically conductive by doping with AsF_5 for example[16].

In contrast to poly(phenylene sulfide)s, very little work has been devoted to poly(thienylene sulfide)s derivatives in which the aromatic ring is thiophene, probably because of the low thermal resistance of the latter.

POLY(POLYSULFIDE)S

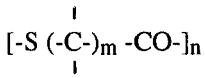
Poly(polysulfide)s polymers have the general formula :

$$(\text{-R - S}_x\text{-})_n \qquad \text{with} \quad x \geq 2$$

(x is often only an average number of S atoms in the polymer units). The presence of polysulfide linkages leads to good resistance to solvents and fuels, resistance to dissolution for linear polymers and to swelling for cross-linked polymers. They have good resistance to environment and good low-temperature properties. Most of these specialty elastomers had been commercially produced by Thiokol Company and therefore the "Thiokol" name is currently used to denominate these materials. A new family of low molecular weight polymers bearing thiol end groups has been produced and used mainly as sealants in glass-insulation industry. Developments and applications of all these polymers has been extensively reviewed[17,18]. The industrial synthesis of high-molecular-weight poly(polysulfide)s involves a complex technique of polycondensation of sodium polysulfide with a dichloro derivative.

POLYTHIOESTERS

Polythioesters form an intermediate family of polymers between polyesters and polyamides.



$$[-S\,(-\underset{|}{\overset{|}{C}}-)_m\,-CO-]_n$$

These polymers has attracted the interest of scientists in the 1950s but none of the prepared polymers were commercialized. Although some of their properties may be more interesting than those of the corresponding polyesters, they are somewhat unstable towards alkalis and also the starting materials of their synthesis (acid chlorides, dimercaptans) are more expensive than those used in the polyester synthesis (diacids, glycols). They can also be prepared by ring-opening polymerization of corresponding thiolactones[1,2,3,19].

POLYTHIOCARBONATES AND RELATED POLYMERS

A series of polymers having the following structural units

$$-O-\underset{\overset{\|}{O}}{C}-S- \qquad -C-\underset{\overset{\|}{S}}{C}-O- \qquad -S-\underset{\overset{\|}{O}}{C}-S- \qquad -S-\underset{\overset{\|}{S}}{C}-S-$$

<u>trivial name</u> : thiocarbonate dithiocarbonate trithiocarbonate

has been prepared by polycondensation or ring-opening polymerization methods.

Miscellaneous polymers containing -NH- functional groups such as poly(carbomoyl sulfenamides) are also known.

POLYSULFOXIDES

Polymers containing sulfoxide group -SO- in the main chain are not easily obtained by direct synthesis. They are mainly synthesized by controlled oxidation of polysulfides.

POLYSULFONES

Polymers containing sulfonyl groups in the main chain have important applications.

$$(\text{-R - SO}_2\text{-})$$

Poly(aliphatic sulfone)s are prepared by copolymerization of sulfur dioxide with unsaturated monomers and are often called olefin-sulfur dioxide copolymers[20]. They are thermally unstable and give on irradiation volatile components (olefin and SO_2). This property is utilized in their application as resists polymers in microelectronic devices.

On the contrary poly(arylene sulfone)s are thermoplastics with high performance retaining good mechanical properties at high temperatures. Different polysulfone plastics were produced since 1965 on commercial scale by different companies (3M, Union Carbide, ICI,...). They can be prepared by Friedel-Crafts reaction of sulfonyl halides with arylene compounds but this method is not economical and presently commercial products are prepared by a Williamson reaction between a bisphenol salt and 4,4'-dichlorodiphenylsulfone for example in a dipolar aprotic solvent such as DMSO or 1-methyl-2-pyrrolidone at elevated temperature[21]. Poly(arylene sulfone)s are clear, rigid thermoplastics with glass-transition temperatures in the range of 180 - 250°C. They maintain excellent mechanical properties over a wide temperature range after a long exposure and in wet conditions. Therefore, they are used in medical and food applications requiring repeated cleaning and sterilization, but they have also electrical and electronic applications and are used as membrane supports.

POLYSULFONAMIDES

Polysulfonamides bearing -NH-SO_2- functional group may be obtained by interfacial polycondensation between disulfonyl dichlorides and diamines and also by ring-opening of cyclic sultams. They have generally melting points lower than those of polyamides.

POLYSULFONATES

Aromatic polysulfonates having the sulfonate ester group $-SO_2-O-$ in the main chain may be easily obtained by polycondensation of aromatic diphenols with aromatic disulfonylchlorides. These polymers have good physical, chemical, thermal properties and are hydrolytically stable at room temperature. They are useful as coatings and adhesives. Wholly aliphatic polysulfonates are prepared from cyclic sulfonates by ring-opening polymerization.

OTHER MISCELLANEOUS POLYMERS

Among other miscellaneous original polymers, we just want to mention :

Organometallic polymers containing S in the chain

Good examples are polymers obtained by polycondensation of Ti, Zr or Hf dicyclopentadienyldichloride with aromatic dithiols[22].

Poly(sulfur nitride)

Poly(sulfur nitride) $(-N-S-)_n$ is obtained by spontaneous polymerization of disulfur dinitride (S_2N_2) at room temperature. This polymer is diamagnetic and has semiconductor properties[23].

GENERAL METHODS OF SYNTHESIS OF S-CONTAINING POLYMERS

Although each of the families of polymers described before has its own particular ways of preparation it is possible to define five general methods of synthesis.

POLYCONDENSATION

The polycondensation reaction is the most wide method of preparation of polymers containing sulfur in the main chain.

The polycondensation reaction proceeds with elimination of a small molecule which can be halogen salt or halogen acid.

Reactions with metallic sulfide salts

Dihalogenenoalkanes reacting with sodium or potassium sulfide at 60°C in a mixture of water/ethanol yield very easily poly(monosulfide)s (24). High molecular weight polymers are obtained in phase-transfer conditions (25).

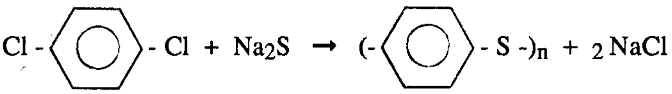
$$n\,Br - R - Br + {}_nNa_2S \rightarrow [-R - S-]_n + 2n\,NaBr$$
$$R = (CH_2)_x \qquad x = 2, 4, 6, 8, 10$$

In the industrial synthesis of poly(polysulfides) the corresponding dihalide is added slowly to a concentrated solution of sodium polysulfide at 70°C.

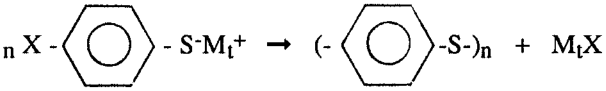
$$n\,Cl - R - Cl + n\,Na_2S_x \rightarrow [-R - S_x]_n + 2\,n\,NaCl$$

Sodium polysulfide is generally prepared by reacting sulfur with sodium hydroxide. The process is in fact much more complex and requires emulsifiers and nucleating agent[17,18].

As already mentionned industrial poly(phenylene sulfide) is prepared according to the same basic scheme by reacting p-dichlorobenzene with sodium sulfide in a polar solvent at elevated temperature[12,15].



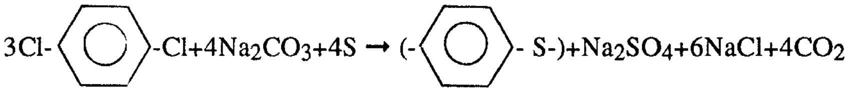
Many works were devoted to elucidate the kinetics and the mechanism of this apparently simple reaction[26-29]. The same linear polymer may be obtained by self-condensation reaction of metalthiophenoxides.



where M_t = Li, K, Na, Cu, ... and X = F, Cl, Br, I.

The reaction is carried out at 200 - 250°C under nitrogen in the solid state, in a slurry or in pyridine solution[30,31]. Depending on the conditions soluble or insoluble polymers are obtained. Random and block can be prepared[32].

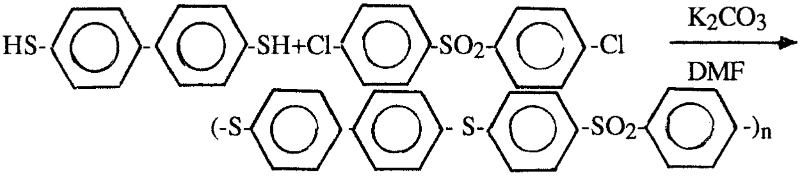
It is worthy to mention here that one of the first simplest methods of preparation of poly(phenylene sulfide) was realized by Macallum in 1948 by polycondensation of dihalogenobenzenes with sulfur in the presence of alkaline carbonate at high temperature[33].



The polymerization is believed to proceed in a first step by formation of metal sulfide.

Methods using dithiols

Dihalogeno aromatic compounds can be reacted with dithiols in the presence of a base, usually K_2CO_3, operating in high boiling solvents, e.g., DMF, DMSO, ... at high temperatures[34].



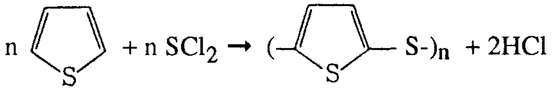
Alternating disulfide copolymers may be obtained when using disulfenyl chloride derivatives(35,36).

$$ClS-R-SCl + HS-R'-SH \xrightarrow{-HCl} (-S-R-SS-R'-S-)_n$$

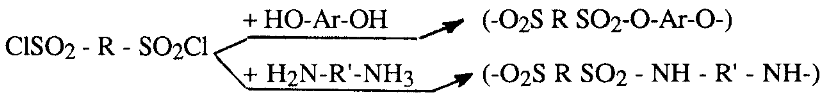
Synthesis using various sulfur halides

Two examples are given :

The first allow to prepare poly(thienylene sulfide) by reacting sulfur chloride with thiophene at room temperature in the presence of magnesium oxide as an acid acceptor[37].



The second method deals with preparation of polysulfonates[38] or polysulfonamides[39,40] by reaction of disulfonyl halides with the corresponding diphenols or diamines.



$$ClSO_2-R-SO_2Cl \xrightarrow{+HO-Ar-OH} (-O_2S\ R\ SO_2-O-Ar-O-)$$

$$ClSO_2-R-SO_2Cl \xrightarrow{+H_2N-R'-NH_3} (-O_2S\ R\ SO_2-NH-R'-NH-)$$

Polyaddition reactions

These reactions are similar to polycondensation reactions but without elimination of small molecules. Dithiols may be reacted with diolefins or diynes using free-radical initiators or by radiation. For diolefins the best results were obtained by operating in emulsion using redox initiators[41].

$$HS-R-HS+CH_2=CH-R'-CH=CH_2 \xrightarrow[rad.]{} (-S-R-S-CH_2CH_2R'-CH_2-CH_2-)$$

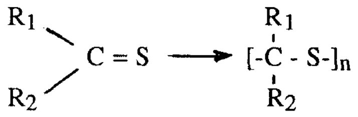
The olefinic double bound may be activated by a sulfonyl group (R' = SO_2) and thus polysulfide-sulfone products are obtained[42]. When using diynes one obtains unsaturated polymers[43]. Finally a monothiol monoolefin, such as 3-vinylbenzenethiol polymerizes spontaneously to give poly(thio-1,3-phenylene ethylene)[44].

STEP GROWTH REACTION

Few S-containing polymers have been obtained by opening of C = S double bound or by copolymerization of an olefin with a sulfur compound.

Polymerization of Thiocarbonyl Compounds

Linear polymers of thioaldehydes and thioketones are obtained by anionic initiation of the corresponding monomers.



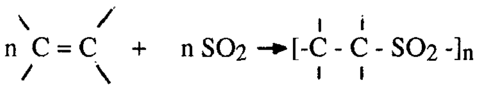
$$R_1R_2C=S \longrightarrow [-\overset{R_1}{\underset{R_2}{C}}-S-]_n$$

with R_1 or R_2 = H, F, Cl, CH_3, Ph, CF_3

In the case of fluorine thiocarbonyl compounds the molecular weight of polymers is strongly affected by the polymerization temperature. Thiocarbonyl fluoride can also be radically copolymerized with a series of ethylenic monomers[10].

Copolymerization of Unsaturated Monomers With SO_2

The reaction product of free-radical polymerization between an olefin and SO_2 is a polysulfone. A number of publications and good reviews were devoted to the study of "olefin-sulfur dioxide" copolymers[20,45,46].



$$n\,C=C + n\,SO_2 \longrightarrow [-C-C-SO_2-]_n$$

A characteristic of this reaction is the existence of a "ceiling" temperature, T_c, above which the polysulfones are thermodynamically unstable. Ceiling temperatures are comprised between 25 and 100°C[47].

Alternating copolymers of 1 : 1 structure were obtained with aliphatic (open chain and cyclic) olefins, 1,3-dienes and monosubstituted acetylenes.

Not all unsaturated monomers are able to copolymerize with SO_2 : highly substituted olefins, α-methylstyrene,vinylpyridines, acrylonitrile, methylmethacrylate and some others do not react with SO_2, which was explained by the existence of very low ceiling temperatures, steric hindrance and electronic effects.

OXIDATION METHODS

These methods may evidently be applied for the preparation of polysulfoxides and polysulfones starting from the corresponding polysulfides.

In the case of polysulfoxides a controlled oxidation using hydrogen peroxide (or other oxidizing agent) is required[48,49]. Poly(methylene sulfone)s can be obtained by oxidation of the corresponding polysulfides with hydrogen peroxide in concentrated formic acid[50]. The oxidation of aromatic dithiols leads to poly(arylene disulfide)s[51].

RING-OPENING POLYMERIZATION

The polymerization of cyclic monomers possessing enough ring-strain can occur via an anionic, cationic, coordinated anionic and more exceptionally radical mechanism.

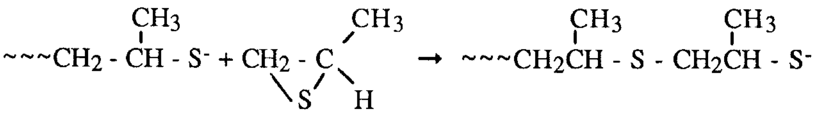
In the cyclic monosulfides series, only three - and four - membered monomers, i.e., thiiranes and thietanes, are able to polymerize. The ionic polymerization of these monomers was extensively studied and detailed reviews are available[8,52,53].

Anionic Polymerization

The most useful method to obtain high polymers from 3 and 4-membered cyclic sulfides is anionic polymerization which leads generally to the so-called "living" polymers without any oligomer formation. Alkali metals, alkali metal complexes with aromatic hydrocarbons, alkyllithium compounds, thiolates, alcoholates, amides, carboxylates etc have been used as initiators.

The first high polymer was obtained from ethylene sulfide (thiirane)[54]. It was crystalline and insoluble in most of the solvents therefore all the detailed studies of mechanism of polymerization were further done on propylene sulfide (methylthiirane).

The propagation occurs via thiolate anion by exclusive attack of the less-substituted carbon atom :



The existence of living polymers (absence of transfer and termination reactions) was demonstrated by Boileau and Sigwalt with the most reactive initiators[55]. The degrees of polymerization are thus determined by the values initial concentrations of monomer and initiator with DP = [M] / [I] for monofunctional initiators and DP = 2 [M] / [I] for difunctional initiators.

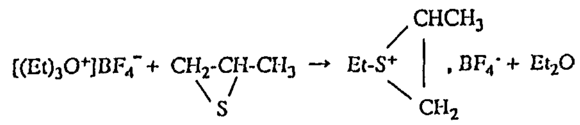
The degree of dissociation of growing centers into free ions were estimated and from kinetic studies the individual propagation rate constants on ion-pairs ($k_p^{\pm}$) and on free ions (k_p^-) were determined. In the case of initiation with carbazylsodium the free ions are about 1000 times more reactive than the ion-pairs[56]. However, when sodium is solvated with cryptands the ion-pairs become more reactive than free ions ($k_p^{\pm} / k_p \sim 2$)[55]. In the case of initiators such as lithium alcoholates polymers containing di and trisulfide linkages are formed due to the elimination of olefin during the polymerization process[57]. Due to the living character of the polymerization, the synthesis of large number of block copolymers was possible either between different thiiranes but also with ethylenic (styrene, methylmethacrylate, isoprene, butadiene, vinyl-2-pyridine, ...) or cyclic (oxirane) monomers[8,53].

The polymerization of thietanes was much less studied. High polymers of thietane have been obtained[58]. The polymerization of 2-methylthietane with butyllithium does not proceed via thiolate active end, but via carbanion[59].

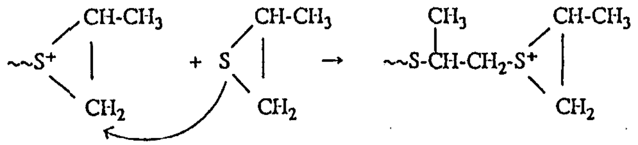
Four, six and seven-membered cyclic thiolactones and also cyclic sulfonates can be polymerized by various anionic initiators (amines, tBuOK, alkylammonium versatate, BuLi, etc...) giving high polymers. The mechanisms of these polymerizations were not extensively studied[2,3,8].

Cationic Polymerization

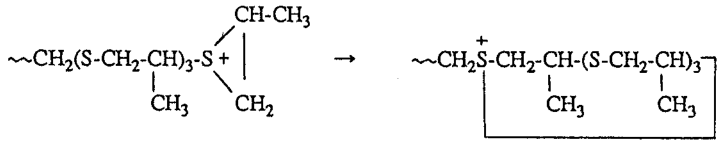
Thiiranes and thietanes are readily polymerized under the influence of cationic initiators such as strong acids, Lewis acids, strong alkylating agents. Extensive kinetic and mechanistic studies were realized by Goethals and his group. With triethyloxonium tetrafluoroborate the mechanism implies the formation of a three-membered ring sulfonium salt in the initiation reaction[60]



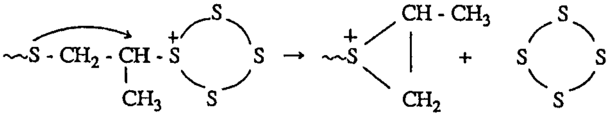
followed by propagation with a nucleophilic attack of the monomer on the α-carbon atom of the cyclic sulfonium salt.



An intramolecular first-order termination reaction between the growing chain and a sulfur atom leads to the formation of twelve-membered ring oligomers.



The terminated polymer reinitiates the polymerization of the remaining monomer or of a freshly added new portion of monomer.



Thus, a characteristic features of the cationic polymerization of thiiranes is the formation of cyclic oligomers during polymerization and after the completion of the latter[61]. Mostly cyclic dimers and tetramers are formed. In the case of cis and trans dimethylthiiranes seven-membered cyclic trithiepanes containing a disulfide function with various structures were formed[62].

For thietanes, the mechanism is similar to the one described for methylthiirane, but the termination is different involving a second-order reaction between the active centers and any sulfur atom of the polymer chain. This termination is irreversible and leads to limited yields that depend on the ratio k_p/k_t[9]. For bulky disubstituted thietanes this ratio may be elevated (~450) and in that case the polymerization is not far from a "living" system. Block copolymers were obtained when initiating the polymerization of thietanes with living polytetrahydrofuran[63].

Other cyclic monomers like cyclic disulfides, trithiane, oxathiolanes may be polymerized in a cationic way.

Radical Polymerization

Only one example of radical polymerization of cyclic sulfur compounds is known: tetrafluorothiirane is polymerized with nitrogen difluoride, N_2F_2, at - 60 - 70°C at 1000 bars, and at room temperature under UV irradiations with bis(trifluoromethyl) disulfide[64]. Copolymerization with propylene was also achieved.

STEREOCHEMICAL ASPECTS RELATED TO POLYSULFIDE POLYMERS

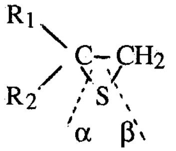
Substituted cyclic monomers may contain one or several (usually no more than two) asymmetric centres in their molecules.

Chiral monomers bearing one asymmetric centre in the ring presents two enantiomers of R and S type. Chiral monomers with two vicinal asymmetric centres may be of diastereoisomeric structure (R - R) and (S - S) or with meso, achiral (R - S) structure.

Thus interesting stereochemical problems occur during the polymerization of such monomers, but also differences in properties appear depending on the structure of the polymer chain and the nature of monomeric unit. These aspects will be briefly discussed now and be limited only to the case of thiiranes which are the most studied of these monomers.

RING-OPENING REACTION

For monosubstituted monomers the C-S bond scission may occur in α- and β-position.



In the case of β-scission the asymmetric centre is untouched and the configuration of the asymmetric carbon atom in the repeating unit in the polymer chain remains identical to that of the monomer molecule. On the contrary in the case of α-scission, the asymmetric carbon atom in inverted at ring-opening reaction introducting in the macromolecular chain a repeating unit of opposite configuration.

Anionic and anionic coordinated initiators open in β-position (retention of configuration) while cationic initiators open partially in α-position (inversion of configuration)[65].

STEREOSPECIFIC POLYMERIZATION

In stereospecific polymerization stereoregular polymers (isotactic) are prepared, i.e., macromolecules formed of only one enantiomeric stereorepeating unit (poly R or / and poly S). Starting from a racemic monomer mixture (R,S) two situations are possible :

Enantiosymmetric (or stereoselective) process

In this process using an achiral stereospecific initiator a racemic polymer mixture is obtained from an initial racemic mixture of enantiomers. Example :

R,S (propylene sulfide) → poly(R-propylene sulfide)+poly(S-propylene sulfide)

The products of hydrolysis, alcoholysis, etc... of organometallic compounds such as $ZnEt_2$, $CdMe_2$ are effective initiators for this purpose. Diethylzinc/water was the first initiator found to produce crystalline high-molecular weight poly(propylene sulfide)[66]. In fact, this system is only partly stereoselective (60 % of the whole polymer is isotactic). The highest stereoregularity was obtained using cadmium tartrate as initiator[67]. In order to prove that the crystalline polymer contains both enantiomeric macromolecular chains, optically pure polymers of both configurations were prepared by polymerization of the corresponding enantiomers. Then a synthetic mixture of these polyenantiomers and polymers prepared with $ZnEt_2$-H_2O system were chromatographied other a column with a chiral support and fractions of opposite signs to each other were obtained in both cases[68].

Owing to the observed fact that isotactic polymer chains are formed, the presence of two enantiomorphic sites R* and S* in the initiator was proposed, each of the sites polymerizing selectively one of the enantiomers. Such a mechanism based on the steric control by enantiomorphic sites involves a coordination-insertion process and is called "anionic coordinated"[65].

The stereoselective character of a polymerization (% of pure isotactic fraction formed) is depending on the nature of the initiator, but also on the nature of the monomer. For example monomers with bulky substituents, such as t-butylthiirane give perfectly isotactic mixtures with $ZnEt_2$-H_2O initiators[67].

Enantioasymmetric (or stereoelective) process

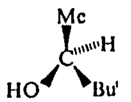
Optically active initiators, having chiral ligands associated with the metal, contain sites with one predominant chirality. Such initiators can cause the preferential polymerization of one of the enantiomers from a racemic mixture. In the course of the reaction the unreacted monomer is continuously enriched in the enantiomer of opposite configuration. In the ideal case only one enantiomer is preferentially polymerized corresponding to the reaction :

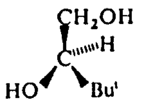
R,S (propylene sulfide) → poly(R-propylene sulfide) + (S enantiomer)

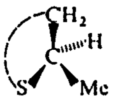
Such a process was called "stereoelective" by Pino et al.[69] in the case of polymerization of olefins. The "stereoelectivity" defined by the relative rate of consumption of the enantiomers, e.g. k_R / k_S, is usually not total. In this respect, it was found by Spassky, Sépulchre and Sigwalt[8,70] that thiiranes were particularly interesting monomers allowing stereoelectivities much higher than oxiranes, β-propiolactones or olefins. The stereoelectivity depends on the nature of initiator, the bulkiness of substituent in the monomer[71]. Effective initiators were obtained by reacting $ZnEt_2$ with chiral diols, e.g., R(-) 3,3-dimethyl-1,2 butanediol (stereoelectivity k_R / k_S = 2.4 for propylene sulfide).

The stereoelectivity can be increased by adding chiral additives or working in chiral solvents (k_R / k_S up to 4) [71]. However, the best result was obtained by Sépulchre et al. when using as chiral ligand (S)-binaphthol. Zinc binaphtholate showed a stereoelectivity $k_S/k_R \sim 20$, which means that at half of conversion, the unreacted monomer was enriched in 90 % with R-enantiomer and at 67 % conversion a monomer 99 % pure R was isolated[72]. This initiator however did not give such good results with other monomers, for whom another perfect "host-guest" situation has to be found.

As concerning the chiral choice, it appears that it obeys to a precise homochiral relation rule. The initiator polymerizes preferentially the enantiomer which has the same spatial configuration as the chiral ligand in the initiator. This choice is named "homosteric". An example of a homosteric relation is shown below :







This homosteric choice is quite general and was found to fit for different zinc initiators prepared in defined conditions from chiral diols or alcohols for various monomers including thiiranes, oxiranes and β-propiolactones[73].

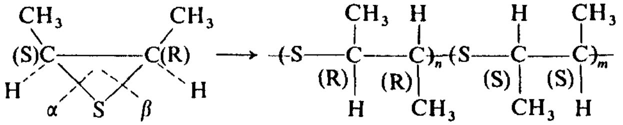
All the initiators described above are heterogeneous systems which forms aggregates and the composition of which is expressed by :

$[R\,Zn\,OR^*]_x \qquad [R^*O\,Zn\,OR^*]_y \qquad R^*$ = chiral moiety

The homosteric choice occurs when $x/y < 1$. However, when $x/y > 2$, the choice of the opposite enantiomer was found and the process was called "antisteric"[77]. Recently, soluble chiral initiators based on cadmium cysteinates were used by Dumas et al. for polymerization of racemic propylene sulfide. The stereoelectivity observed up to now is not very high (k_S / k_R = 1.4), but the initiator consumption was quantitative and living polymers were obtained[75] which permitted to follow the variation of stereospecificity along the polymerization. An inversion of sign of the preferentially chosen enantiomer with the temperature has been observed[76]. Similar phenomenon was also reported in the polymerization of t-butylthiirane using heterogeneous initiators[77].

Enantiogenic process

When a meso type monomer, e.g., cis-dimethylthiirane, with two vicinal asymmetric carbons of opposite configurations, is polymerized, the resulting polymer contains -RR- and -SS- type configurational units (due to inversion of configuration at ring-opening reaction).



Momtaz et al. using chiral initiators similar to those employed in stereoelective polymerization of racemic thiiranes have prepared optically active polymers from cis-dimethylthiirane[78]. The best results, i.e., enantiomeric enrichment m/n ~ 11,were obtained using zinc (S)-binaphtholate as initiator in the presence of tetrahydrothiophene[79,80]. It is clear that the chiral initiator is able to distinguish the configuration of an asymmetric carbon atom and to proceed with a regiospecific attack of the cycle in agreement with homosteric-antisteric type relation.

This process, which favorizes the preparation of a polymer enriched in one enantiomeric unit, was called "enantiogenic" and it is equivalent to an "asymmetric synthesis of polymers".

Cyclohexene sulfide, another meso monomer, was also able to produce optically active polymers when polymerized with the same chiral initiators[80].

PHYSICOCHEMICAL PROPERTIES

The methods of synthesis described above are able to produce macromolecules with various distributions of enantiomeric units in the chain. The following ones are interesting to be compared from the point of view of the variation of physical properties.

[1]	-RRSRSRRSSS-	random copolymer
[2]	-RRRRSRSRRRR-	enantiomerically enriched copolymer
[3]	-RRRRRRRRRRR-	polyenantiomer
[4]	-RRRRRRRRRRRR- + -SSSSSSSSSSS-	racemic polymer mixture

Atactic monosubstituted polythiiranes of structure [1] are amorphous. The appearance of a melting point, i.e., crystallinity, necessitates a certain enantiomeric enrichment, for example a distribution around S/R = 90/10 in the case of poly(t-butylthiirane). Then, the m.p. increases linearly with enantiomeric excess and a sharp rise is observed[81]. In fact, the presence of enantiomeric units of opposite configuration equals to the addition of impurities which decrease the length of the crystallizable sequence. The latter must be of ca. 9 - 10 units for poly(t-butylthiirane). The melting point of almost pure isotactic poly((S)-t-butylthiirane) is 160°C. It was interesting to compare the properties of this pure polyenantiomer with a racemic mixture of two polyenantiomeric chains (poly R + poly S). The latter may be obtained by stereoselective polymerization. Dumas et al.[82] observed that this polymer has an enhanced m.p. close to 205°C and that physical properties (solubility, density) were quite different. It was also shown that the crystalline structure of the racemate differs of that of polyenantiomer[83]. On the other hand in the case of poly(methylthiirane) the properties of polyenantiomers and of the racemic mixture were identical as well as their crystalline structure[84].

These two types of behaviour were explained by Tadokoro on the basis of differences in the type of optical compensation of the two polyenantiomeric chains[85]. In the case of poly(methylthiirane) the racemic mixture is formed of crystallites of chains of both chiralities and therefore the properties are identical. In the case of poly(t-butylthiirane) the racemate forms a racemic lattice with a structure different of that of the polyenantiomer and therefore the crystalline properties, the density, etc... are different. Poly(t-butylthiirane) was the first example in the literature reported for such a behaviour in polymers. Presently, several examples of substituted poly(β-propiolactones) and polylactide are known[86,87]. Thus, the properties of stereocopolymers may substantially vary with the enantiomeric composition and new materials with improved properties may be expected from such stereocomplexes.

CONCLUSION

This short review tentatively try to enlighten the broad interest of the very wide variety of S-containing polymers. Several of the described materials have industrial applications, many of them have a potential one and many others are interesting by their contribution to the fundamental science.

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