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Contemporary State of the Problem of the Polymerisation and Copolymerisation of Alkene Sulphides [Epithioalkanes]

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Studies of the polymerisation and copolymerisation of alkene sulphides, including those published in 1971, are reviewed. The literature is classified according to the nature of the action of the catalytic systems—polymerisation under the influence of anionic and cationic excitants, modified organometallic compounds, and charge-transfer complexes. A separate chapter gives the results of studies on the copolymerisation of thio-oxides. 176 references.

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I. INTRODUCTION

The polymerisation and copolymerisation of cyclic sulphides (alkene sulphides, thio-oxides, episulphides, thiirans, thioethanes) has only recently attracted the attention of investigators, but every year the number of papers dealing with these problems increases. The problem is of interest both theoretically as regards the formation of polymers by the opening of heterocycles, and also from the standpoint of the practical use of a new class of polymers which contain monosulphide bonds in the main chain. Unlike their oxygen analogues—the cyclic oxides, the polymerisation of which has been studied in sufficient detail and many polymer compositions based on which have found wide practical application—information about the polymerisation and copolymerisation of cyclic sulphides, and also the physicochemical properties of the polymers formed has been unsystematic until recently and in several instances only qualitative.

Nevertheless, the available published information shows that the formation of a polymeric chain in opening cyclic thio-oxides is quite unique and the crystalline and rubbery polymers and copolymers which are formed exhibit a series of valuable working properties, above all increased radiation resistance, high adhesion and dielectric properties, specific in relation to various solvents, increased resistance to oxidants, etc.

A feature of the behaviour of cyclic sulphides, and in particular of thiirans, in nucleophilic and electrophilic reactions, which appears in ionic polymerisation, is connected with the specific structure of their molecules, examined in detail in several contemporary reviews[1-5]. In this connection we thought it undesirable in the present review to state the physicochemical properties of the cyclic sulphides and compare them with the properties of other small heterocyclic compounds.

II. POLYMERISATION OF ALKENE SULPHIDES

Over a long period of time the existence of thiirans was demonstrated only on a basis of a study of the structure and composition of the polymeric products formed in attempts to synthesise them by various methods[6,7]. The ease of opening of the ring of the α-thio-oxide to form polymeric compounds led Grishkevich-Trofimovskii[7] to conclude that they could not exist in the free state. Later Délépin, who was the first to succeed in synthesising and isolating the simplest α-thio-oxides in the pure state, showed their extreme ability to polymerise under the influence of various agents.

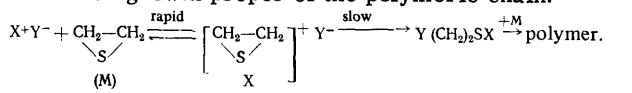
After the development of simple universal methods of synthesising the thiirans from oxides[12], and cyclic carbonates[13,14] interest in this class of compound increased greatly and in addition to the investigation of the physicochemical properties of the thio-oxides papers also appeared on the study of their polymerisation—mainly the simplest and most accessible thiirans—ethylene sulphide [thiiran or epithioethane (Ed. of Translation)] and propene-sulphide [1,2-epithiopropane (Ed. of Translation)]—which are relatively stable when pure at low temperature[4].

An attempt to polymerise thiirans under the influence of radical type initiators did not give positive results[15,16]; only for perfluorinated α-thio-oxides was the possibility of polymerisation under the influence of free radicals demonstrated, brought about by the breaking of a C–S bond[17]. The first papers dealing with the study of the ionic polymerisation of thiirans appeared in 1954, but systematic investigations in this field began to appear in the sixties. The Table gives information about the polymerisation of alkene sulphides in the presence of various catalytic systems. The most interesting investigations dealing with the polymerisation of the thio-oxides can be classified into four main groups according to the type of catalytic system used: polymerisation under the influence of anionic inducers, modified organometallic compounds, cationic inducers, and charge-transfer complexes. A separate section gives the principal results of work on the copolymerisation of alkene sulphides.

This classification is extremely provisional because in the variety of initiating systems often within the framework of qualitative observations it is difficult to draw a boundary between the individual groups of inducers according to the mechanism of their action. Thus, for the α-oxides[86] and α-thio-oxides[87-89] it is known that the $Zn(C_2H_5)_2-H_2O$ system can be cationic or coordination-anionic, depending upon the ratio of the components and in excitation polymerisation but in the induction polymerisation of propene sulphide with a charge-transfer complex the nature of the initiation and growth processes of the polymeric chain are different.

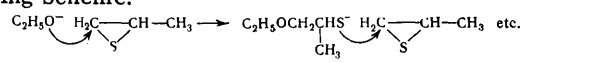
1. Polymerisation of Alkene Sulphides under the Influence of Inducers of the Anionic Type

The polymerisation of alkene sulphides in the presence of Lewis bases can be represented as a succession of reactions: (1) the addition of a molecule of the monomer to the inducer with the formation of an active centre, and (2) the successive addition of the monomer to the mercaptide formed—growth proper of the polymeric chain:



Reactions of this type are close to the break-free polymerisation of monomers of the vinyl series. The principle of the polymerisation of α-thio-oxides which corresponds to ideas about the "living" polymers, was described in a series of papers [16,22,23,38–42,57,70,74,90].

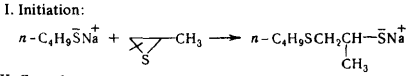
Marvell and Weil [34] obtained low-molecular-weight polypropene sulphide poly(epithiopropane) under pressure at 95–100°C in the presence of an alcoholic solution of sodium ethoxide and represented this process by the following scheme:



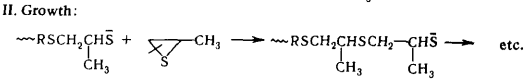
Culvenor and coworkers [91] also associate the polymerisation of ethylene sulphide under the action of NaOH or other alkali agents (NaX) with the formation of $NaSCH_2CH_2OH$ (X); they showed that the α-thio-oxides do not polymerise when the molecule of the attacking agent is constructed so that the product of its condensation with one molecule of the monomer is a stable cyclic compound (for example, trithiocarbonate in the reaction of ethylene sulphide with thiourea or thiocyanates).

In 1964 Ishii and coworkers [35], in studying the polymerisation of propene sulphide (PS) in the presence of various organometallic compounds showed that the alkoxides effective for the induction of the polymerisation of α-oxides (sodium, iron, and titanium ethoxides; aluminium 2-propoxide, Pr^i_2AlOH) are not effective in the polymerisation of episulphides and suggested that Marvel's results [34] are due to the presence of traces of moisture in the system and hydrolysis of the alkoxide. In the same work Ishii showed that sodium, cadmium, zinc, copper, nickel, cobalt, and iron mercaptides at 0–80°C are capable of bringing about the polymerisation of PS with the formation of viscous oils. The use of polar solvents increased the rate of the process. They used infrared spectroscopy to show the presence of C=C groups in the polymer, which allowed them to propose a scheme for the polymerisation of PS by an anionic mechanism which includes a chain transfer reaction:

I. Initiation:

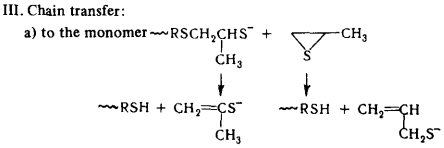


II. Growth:

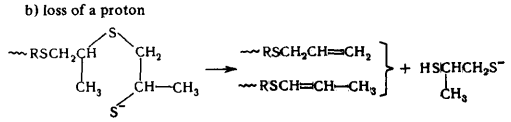


III. Chain transfer:

a) to the monomer



b) loss of a proton



The same investigators studied the polymerisation of PS under the influence of $Al(C_2H_5)_3$, $Zn(C_2H_5)_2$, and $Al(C_2H_5)Cl$ [35] at 0°C and showed that the presence of water in the system reduces the catalytic activity of the inducer.

Catalytic systems used for initiating the polymerisation of alkene sulphides.

Initiating system	Monomer	Reference
Ultraviolet, γ-radiation, peroxides diazo-compounds	CHS, perfluorinated and unsaturated episulphides	17–19
Organic and dilute mineral acids	ES, PS, BS, CHS, TE, TECH	9–11, 16, 20, 21
Lewis acids: BF_3, PF_5, SbF_5, $BF_3O(C_2H_5)_2$; $AlCl_3$; $TiCl_4$, AsF_5	PS, ES, TE, 7-TBCH, 6-TBCH, 3,3-DMTE, CHS	19–31
Onium salts: $R_3\overset{+}{O}-\bar{B}F_4$, $R_3\overset{+}{S}-\bar{B}F_4$	PS, TE, DMTE, 7-TBCH, 6-TBCH	23, 25, 26.
Metals, their oxides, and hydroxides (M = Na, K, Mg, Al, Ca, Fe, Co, Ni, Sr, Pb etc.)	ES, PS, BS	16, 22, 32, 33
Alkoxides (M = Na, K, Al, Fe, Zn)	PS, SS, ES	22, 34–37
Mercaptides (M = Na, K, Fe, Co, Cu, etc.)	ES, PS, SS	32, 35, 36, 38–48
MR, MRX	PS, ES, OS, TE, IBS	19, 22, 23, 32, 35, 36, 42, 43, 49–57
MR_2 + modifier (M = Zn, Cd, Mg)	ES, PS, BS, CHS, SS, TE	19, 42, 58–68
AlR_3 + mercaptides (Zn, Cu, Co, Ni, Fe); chelates	PS PS	35 69
Mineral salts of Cd, Zn, Mg, Hg	PS, ES, BS, SS, CHS	9–11, 70–76
Amines, polyamines, pyridine, carbazole, guanidine, hydroxylamine, *o*-aminophenol	CHS, PS, ES	77, 78
$NaNH_2$ and other amides	ES, PS	22, 79, 80
Xanthates, dithiocarbonates, thiocarboxylates of metals	ES, PS, BS	67, 81
$LiAlH_4$	1-OS	82
Charge transfer complexes	PS	83–85

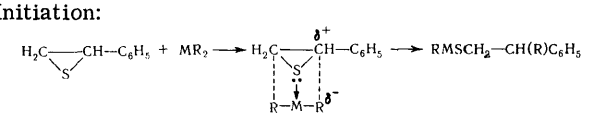
Symbols: ES ethylene sulphide [thiiran or epithioethane], PS propene sulphide [1,2-epithiopropane], BS butene sulphide [1,2-epithiobutane], CHS cyclohexene sulphide [1,2-epithiocyclohexane], SS styrene sulphide [$\alpha\beta$-epithioethylbenzene], TECH thioepichlorhydrin [3-chloro-1,2-epithiopropane], 1-OS 1-octene sulphide [1,2-epithiooctane], IBS isobutene sulphide [1,2-epithio-2-methylpropane], TE thiethane, TBCH thiobicycloheptane, DMTE dimethylthiethane.

From these results it was concluded that the hydrolysis products of organoaluminium compounds are ineffective for the induction of the polymerisation of thio-oxides. In 1968 the same investigators re-examined their previous results and published an article in which they examined in

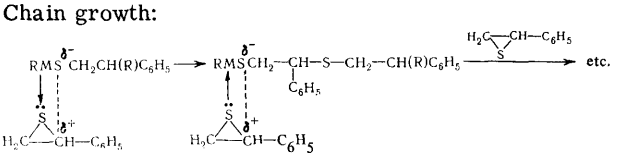
detail the $Al(C_2H_5)_3-H_2O$ system as an initiator of the polymerisation of PS. The results of this work will be considered in the appropriate section.

Nashay and Price[36] studied a large number of catalysts in the polymerisation of styrene sulphide [$\alpha\beta$-epithioethylbenzene], but only the use of triethylaluminium and chlorcadmiumbutylmercaptide at and below room temperature allowed poly(styrene sulphide) with rather high molecular weight to be obtained. It is assumed that chain initiation and growth is neither radical nor ionic in nature and a coordination mechanism is suggested:

Initiation:



Chain growth:



In considering the anionic polymerisation of the PS mention must be made of Kabayashi[70], who first observed that salts of elements of Group IIB, and especially cadmium compounds, give an excellent catalytic effect. CdS, CdO, $Cd(OH)_2$, $CdCO_3$, and $CdSiO_3$ were most active. Whereas zinc catalysts lead to the formation of amorphous, mainly atactic poly(propene sulphide), cadmium sulphides form crystalline polymers which are evidently isotactic ($T_f = 40-45°C$, $Tg = -52.5°C$) with a high value of the characteristic viscosity (up to 10). When cadmium silicates are used, addition of water is needed to increase its activity, which leads to an increase in the molecular weight of the polymer and the rate of the process. Addition of NaOH (up to pH 8) leads to a similar effect. Spectroscopic investigations confirmed the presence in the polymer of the metal used as catalyst. The investigators did not examine the mechanism of the catalytic action of water and sodium hydroxide, but suggested that the polymerisation was stepwise anionic for all types of cadmium salts.

In the presence of the $CdCl_2 + NH_4Cl + K_2S$ [71] or of cadmium or zinc carbonates[72] PS is also polymerised and copolymerised with the formation of high-molecular-weight and oligomeric polymers[73,92].

The studies of Cooper, Morgan, and Wragg[38-41,74] show the special effectiveness of cadmium compounds in the polymerisation of episulphides. The investigators studied the polymerisation of alkene sulphides in the presence of mercaptides, which model the active centres of the process, which is completely reproducible. However, the study of the mechanism and kinetics of the process is hindered by the restricted solubility of mercaptides[36] or by the presence in homogeneous systems of traces of mercaptides which are extremely active chain transfer agents[35].

Wragg and coworkers[38-40] obtained poly(propene sulphide) and poly(ethylene sulphide) of practically any molecular weight by using soluble heavy metal (Zn, Cd, Cu, Ni, Co, Pb, etc.) mercaptides as catalysts. Having studied the initiating capability, of mercaptides of various structures, they showed that the most effective inducers of polymerisation are cadmium and zinc thiolates; the mercaptides $M(SCH_2CH{=}CH_2)_2$ obtained from unsaturated thiols have good solubility, and the dialkayldiaminoalkylthiolates

$$M[SCH(CH_3)-CH_2S-CH(CH_3)CH_2N(n\text{-}C_4H_9)_2]_2$$

dissolve almost instantaneously. They associate the increased solubility of the heavy metal mercaptides with their tetragonal structure, due to the presence in the initial thiol in the β-position of a substituent capable of coordination with a metal. All these compounds are stable in air and the presence of moisture does not affect their activity. Wragg and coworkers arranged the most active cadmium mercaptides in the following series:

$$Cd(SCH_2CH{=}CH_2)_2 \simeq Cd(SCH(CH_3)CH_2NR_2)_2 \simeq$$
$$\simeq Cd(SCH_2CH_2SBu)_2 > Cd(SCH_2CH_2OBu)_2.$$

By carrying out a detailed kinetic investigation, Wragg and coworkers[38-40] showed that polymerisation under the influence of heavy mercaptides proceeds by a "living" chain mechanism with an induction period, the length of which depends on the nature and solubility of the inducer. On the stationary part

$$v_p = k_p\,[\text{alkene sulphide}][\text{catalyst}].$$

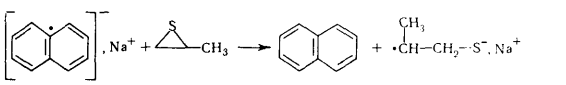
The first order of the reaction with respect to the monomer and the similarity in the growth rate constants in using cadmium mercaptides of various structures show that the coordination of the monomer with a metal does not play a decisive part. However, the latter is supported by the stereospecificity of the inducers used, leading to the formation of a crystalline poly(propene sulphide), and the suppression of polymerisation or a decrease in the rate of the process in the introduction of strong electron-donating additions (amines). As regards the use of aminothiols as polymerisation inducers they did not exclude the possibility of inter-chain interactions, leading to the cross-linking of polymers. The part played by thiols as chain carriers in the polymerisation of thio-oxides was proved convincingly in these studies.

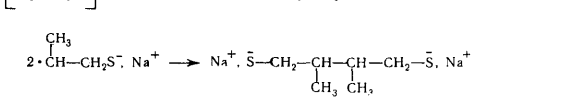
Over a long period there was systematic investigation of the anionic polymerisation of propene sulphide by French scientists led by Sigwalt[22,42,49-55,79].

In the first papers[22,79], which were qualitative, they showed that poly(propene sulphide) of high molecular weight can be obtained by using an anionic type of catalyst—sodium naphthalene in tetrahydrofuran (THF), sodium amide, sodium films. Subsequently, by studying the polymerisation of PS under the influence of the sodium–naphthalene complex in dilute THF solutions[49] they found that the process takes place by a "living" chain mechanism, not complicated by chain breaking or transfer reactions and the mean degree of polymerisation of the polymer formed at any stage of the transformation strictly calculated by the formula:

$$\overline{DP}_n = \frac{\Delta M}{{}^1/_2\,[\text{cat.}]} \quad \left(\text{in which } \frac{\bar{M}_w}{\bar{M}_n} \to 1\right)$$

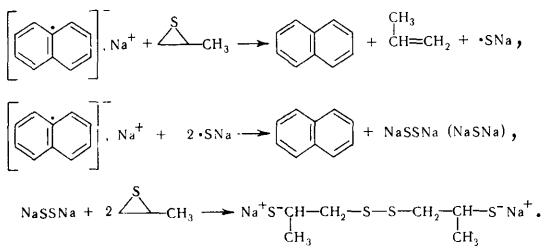
It was suggested[54,55] that the initiation of the polymerisation of PS in the presence of the sodium naphthalene complex takes place by a mechanism according to which, by analogy with vinyl compounds[93], there is transfer of an electron to the monomer with subsequent dimerisation of the anion-radical by the scheme:





Confirmation of this bifunctional mechanism was provided by the almost complete regeneration of the naphthalene (up to 98%). Although the instantaneous disappearance of the naphthalene anion-radical was observed at −78°C, chain growth was noted only above 0°C, which was attributed to the low reactivity of the primary active centre—sodium dimercaptide.

Subsequent kinetic, conductimetric, and spectrophotometric studies of the polymerisation of PS under the influence of the sodium naphthalene complex showed that the initiation is more complex and polymerisation can be effected below 0°C. In later studies[50-52,54] it was observed that the polymerisation of PS in this system is accompanied by the release of propene and the existence of an induction period which is most pronounced at low temperature (−30°C), and which can be avoided by the use of "seed" "living" polymers obtained in the presence of any anionic inducer (sodium naphthalene, sodium mercaptide, sodium carbazyl, or potassium carbazyl)[54]. The characteristic conductometric curves also confirm the slow initiation. On the basis of these results the act of primary interaction of the monomer with sodium naphthalene and the subsequent stages are formulated as follows:



The intermediate active compounds were not identified.

In the range of catalyst concentrations up to 1×10^{-3} M an expression was obtained for the overall rate of the process,

$$v_p = k_p[M][\text{cat.}]^{1/2},$$

where k_p is the overall growth rate constant, and [M] and [cat.] are the monomer and catalyst concentrations respectively. The variation of the rate of the process with the catalyst concentration is linked with the possibility of parallel growth of the polymeric chain into ion-pairs and free ions, present in equilibrium. By use of the Szwarc method[94,95] the individual rate constants of the reactions at free ions and ion-pairs with sodium counter-ions in THF and tetrahydropyran (THP) solution were calculated[54].

The change in the electrical conductivity of the system during the polymerisation of PS in THF [51] and THP [54] solution gave the dissociation constant K_d for the ion-pair S^-, M^+ with counter-ions Na^+, K^+, Li^+, and NR_4^+.[96] The sequence of activities of the counter-ions was found to be opposite to that observed for a carbanion[95], owing to the reduced contribution of the solvating effects. In studying the polymerisation of PS in THF it was found that with an initiator concentration above 1×10^{-3} M the rate of the process is not described by the above equation. This phenomenon is connected with the existence in the system of a series of equilibria involving ion-pairs and free ions:

$$(S_2Na)^- + Na^+ \overset{k_3}{\rightleftharpoons} (S,Na)_2 \overset{k_2}{\rightleftharpoons} 2\,S,Na \overset{k_1}{\rightleftharpoons} 2S^- + 2Na^+$$

where (S,Na) is a thiolate active centre in the form of an ion-pair, $(S_2Na)^-$ an associate of the ion-pair with a free ion, and $(S,Na)_2$ an associate including two ion-pairs.

The existence of associates under these conditions agrees with the departure of the electrical conductivity of the system from linearity in the same concentration region and this was proved by viscosimetric measurements by Morton's method[97] involving comparison of the time of flow of solutions of the reaction mixtures before and after disturbance of the active centres $\sim S^-, M^+$ by the terminating agent (ethyl bromide).

It has been shown[52] that in working with a monofunctional excitant (sodium triphenylmethyl) the regularity of the process is analogous to that in working with sodium naphthalene. It was assumed that bifunctional compounds of the SNa_2 or S_2Na_2 type or their mixtures are also polymer chain initiation agents. The use of sodium and potassium carbazyls as initiators of PS polymerisation[98] allowed a truly monofunctional polymer to be obtained, the formation of which obeys all the kinetic rules established for bifunctional poly(propene sulphide).

Another type of anionic inducer of polymerisation, butyllithium, has been investigated[23,32,43,99]. Under block polymerisation conditions in solution in non-polar solvents the polymerisation of PS under the influence of butyllithium proceeds at a low rate. The introduction of 10 to 70 mole % THF causes a marked increase in the rate of the process. In the temperature range from −25° to +20°C over a wide range of monomer and initiator concentrations the homogeneous process of polymerisation proceeds without an induction period up to complete disappearance of the monomer and is described as a quasi-stationary process with a constantly acting number of active centres and a total activation energy of 11.8 kcal mole^{-1}. The nature of the dependence of the molecular weight on the polymerisation conditions (temperature, concentrations of the initial reactants, degree of conversion) shows that the process takes place with participation of "live" polymeric chains with complete use of the initiator introduced and allows the formula for calculating the degree of polymerisation found for the uninterrupted processes to be used.

However, the investigation of the variation of the molecular-weight distribution (MWD) of poly(propene sulphide) with the extent of conversion and temperature of the reaction, made at various monomer and initiator concentrations and in the absence of a solvent showed the complexity of the process. In every instance the MWD curves were unimodal with an inflexion in the high molecular weight range (Fig. 1) and polydispersity coefficients of $\bar{M}_w/\bar{M}_n \to 1.5$ and $\bar{M}_z/\bar{M}_w \to 1.33$. In the absence of reaction the limit of the polymeric chain growth of the type of distribution of poly(propene sulphide) according to molecular weight was thought to be linked with the presence in the system of "pseudo-rupture" phenomena consisting of the occurrence throughout the entire process of a spontaneous deactivation of the $\sim S^-, Li^+$ active centres, due to the ability of the organolithium compounds to be associated and subsequently reactivated when they react with the monomer. Hence at every moment in the acts of polymeric chain growth only some of the active centres that are formed, and not all the initiator, participate. On the other hand, the fact that irrespective of the conditions under which the polymerisation is carried out the distribution of the macromolecules by size obeys the relation

$$q_w(M) = \frac{(\alpha M^2)e^{-\alpha M}}{\bar{M}_n},$$

where M is the molecular weight of a polymer fraction, $\bar{M}_n$ the number mean molecular weight, and α is either

proportional to M or is a constant ($2/\bar{M}_n$), and the polydispersity coefficients $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_n$ are 1.5 and 1.33 respectively, is thought to show that under the chosen conditions each polymer chain is constructed from two statistically independent polymeric chains growing on a bifunctional active centre, which agrees with the observed values of the number mean molecular weights. Chromatographic analysis of the gaseous products formed showed the identity of the mechanism of interaction of butyl-lithium and sodium naphthalene with PS in THF medium and in the absence of the latter through the sulphur-elimination stage.

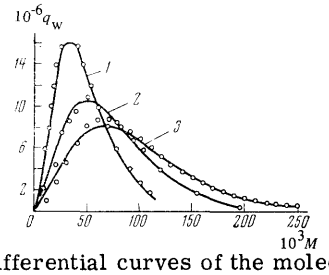


Figure 1. Differential curves of the molecular weight distribution of polypropene sulphide obtained at $[C_4H_9Li] = 4.8 \times 10^{-3}$ M; [PS] = 2.46 M, $t° = -25°C$, in a tetrahydrofuran medium. The experimental points are plotted along curves calculated by the formula

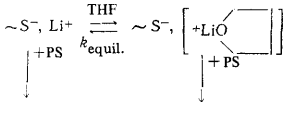
$$q_w(M) = \frac{(\alpha \cdot M)^2 \cdot e^{-\alpha M}}{\bar{M}_n};$$

Conversion, %: *1*) 46.0; *2*) 71.5; *3*) 100.

The main kinetic parameters of the polymerisation of PS were studied at 0°C. In the range of butyl-lithium concentrations from 1×10^{-3} to 1.8×10^{-2} M the order of reaction with respect to the excitant was varied from 1 to 0. The dependence of the rate of polymerisation of PS on its concentration in THF is shown in Fig. 2. The total rate of the process is

$$v_p = k_p[M]^2[\mathrm{THF}]^2[\mathrm{cat.}].$$

It was assumed that the nature of the relation between the polymerisation rate and the concentrations of the initial reagents is determined by the fact that butyl-lithium is present in a medium of two strongly electron-donating agents, of which PS is the more polar ($\epsilon_{PS} = 10.2$, $\epsilon_{THF} = 7.6$), but THF is the stronger complexing agent[100,101], due to the presence in the polymerising system of the equilibrium:



A study of the electrical conductivity of the PS–butyl-lithium + THF system[99] enabled us to draw conclusions about the decisive part played by ion-pairs in polymer chain growth and to find that THF participates in the specific solvation of the low-reactivity contact ion-pair $\sim S^-, Li^+$, converting it into a "loose" (separated by the solvent) ion pair $\sim S^-, [Li^+, THF]$ the reactivity of which is 50–80 times greater than the reactivity of the contact pair.

A study of the copolymerisation of PS with α-, β-, and γ-thio-oxides: ethylene sulphide, thiethane, and thiophan, which are distinguished by the basicity of the heteroatom and the strain of the ring enabled us to answer the problem which is crucial in the growth stage: coordination of the sulphide with the counter-ion or the introduction of complex-bound monomer at the S–Li bond (ring opening, thermal effect). The results of infrared spectroscopy and elemental analysis show that the copolymers are enriched with the component with the more highly strained ring, which is also the determining factor in ring opening under the action of a nucleophilic reagent. However, the retardation of polymerisation on the addition of small amounts of the compounds of greater basicity (thiophan, thiethane) suggests that a significant part is also played by the coordination of sulphide with the counter-ion, which modifies the active centre and shows the kinetics of the process but does not alter the direction of the chain formation. On the basis of the results obtained a coordination-anionic mechanism of polymerisation of the PS under the influence of butyl-lithium is proposed, including stages of initiation, growth, "pseudo-breaking", reactivation, and the corresponding kinetic calculations are given[99].

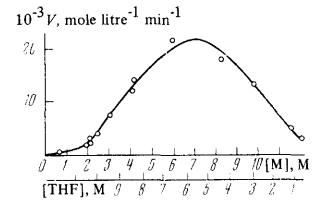


Figure 2. Variation of the rate of polymerisation of propene sulphide with the concentrations of the monomer and tetrahydrofuran at 0°C and $[C_4H_9Li]_0 = 3 \times 10^{-3}$ M.

Some regularities in the polymerisation of PS initiated by $Al(C_4H_9^i)_2Cl$ in benzene and diethyl ether solution have been studied by gas–liquid chromatography[44]. It was shown that polymerisation can be effected at temperatures from −20° to +20°C with an overall activation energy of 11.4 kcal mole^{-1}. Thermogravimetric analysis of the poly(propene sulphide) *in vacuo* and in air showed that the decomposition of the polymer takes place almost entirely in the range 225–320°C, to give propene, ethane, and isopropylthiol and is accompanied by appreciable endothermic effects. No suggestions were made as to the mechanism of the initiation, growth, or breaking of the polymeric chain.

Hence in the opinion of most authors, in the anionic polymerisation of alkene sulphides irrespective of the initial initiator the growth of the polymeric chains is effected by the thiolate anion S^-, M^+. When growth precedes the coordination of the active centre with the monomer, the polymerisation is effected by a coordination-anionic mechanism.

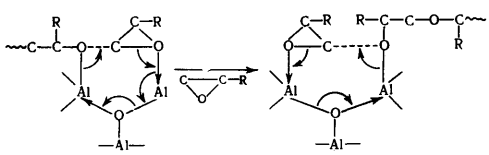
2. Polymerisation of Alkene Sulphides under the Influence of Modified Organometallic Compounds

Catalytic systems based on organozinc and organoaluminium compounds in the presence of cocatalysts are

widely used for the preparation of high-molecular-weight polyoxyethylenes with a high degree of tacticity[58-62,102-113].

Despite the prolonged and serious study of the polymerisation and copolymerisation of alkene oxides under the influence of modified organometallic compounds, the mechanism of their action is far from being explained completely. Whereas in the first studies of Furukawa and Saegusa[102] catalytic activity was attributed to the O–M–O bond, at which coordination of the monomer took place, Colclough and Wilkinson[103] and Vandenberg[104] thought that the growth of the polymeric chain takes place by a cationic mechanism with participation of stable onium ions formed during the interaction of the monomer with the hydrated form of the organoaluminium compound. Many investigators drew conclusions about the "onium" nature of the polymerisation of oxygen-containing heterocycles at AlR_3 + H_2O and $Zn(C_2H_5)_2$ + H_2O systems on the basis of a study of the constants of the copolymerisation of the various oxides and their comparison with results on copolymerisation under the influence of catalysts of typically cationic nature [$BF_3.(C_2H_5)_2O$, $SnCl_4$].[105-108]

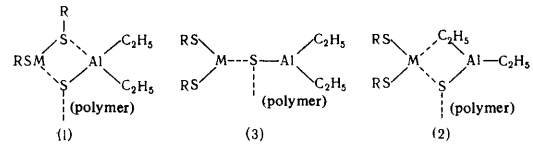
Recently a series of papers by Vandenberg[114,115] and Price[116,117] has reported that the polymerisation of oxides, which leads to the production of regularly constructed crystalline polymers, is due to the coordination of the monomer at an active centre having more than one metal atom:



This was proved convincingly by Osgan and coworkers[118,119] in investigating bimetallic μ-oxoalkoxides as catalysts of the polymerisation of epoxides by an injection mechanism. The part played by electronic and structural factors and also by other cooperative effects in the mechanism of coordinated polymerisation under the influence of the catalysts employed was examined and the possibility of bridging oxygen participating in the monomer addition stage was demonstrated. Some new aspects of the catalysis of the polymerisation of heterocycles by organometallic compounds were examined in a paper published recently by Furukawa[120].

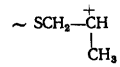
As recent studies have shown, in the presence of various modifying additions the $Al(C_2H_5)_3$ and $Zn(C_2H_5)_2$ systems are active for the induction of directed polymerisation of α-thio-oxides, but we have found only a few publications and these contain extremely limited material[35,63,67,68,70,121-125]. Nevertheless, the results of these studies allow our ideas about the nature of the active centres and the mechanism of polymerisation of the heterocyclic compounds in using organozinc and organoaluminium compounds to be extended.

Coordination leading to a regular structure of the chain and the production of a crystalline polymer were observed by Ishii and coworkers[35] in the polymerisation of PS under the influence of AlR_3, modified with water and various metal mercaptides. They showed that whereas Na, Co, Zn, Ni, and Cu mercaptides form low-molecular-weight amorphous polymers but triethylaluminium both in the absence of additions and in the presence of water is of little effect on the induction of polymerisation, a combination of trialkylaluminium with mercaptides leads to the formation of a high-molecular-weight crystalline polymer. The greatest activity is observed in using iron and cobalt mercaptides. It was found, by the example of $Al(C_2H_5)_3$ + $Co(SBu^n)_n$ and $Al(C_2H_5)_3$ + $Fe(SBu^n)_3$, that on varying the Al/M ratio from 0.5 to 2 the degree of conversion is increased, but the maximal value of the molecular weight ($[\eta] = 2.0$) is reached at the ratio Al/Co = 1.0. This was attributed to the phenomenon of chain transfer from the excess of $Al(C_2H_5)_3$ but the mechanism of this process was not examined. It was assumed that in the initial stage of the polymerisation takes place under the action of $Al(C_2H_5)_3$ but subsequently the polymeric ions coordinate with the metal mercaptide, acquiring form (1), (2), or (3), and polymerisation takes place at the $S^- - M^+$ bond, which ensures stereoregular growth of the chain. Growth of the polymeric chain at complexes of structure (1) and (2) is preferred by the investigators.



The non-stereospecificity of the $Al(C_2H_5)_3$ + $Ni(SR)_2$ system is attributed to the monomeric structure of nickel mercaptides in which the sulphur atoms are arranged non-regularly[126]. Some conclusions drawn in this study concerning the reactivity of the O–M bond were disproved by the French investigators Machon and Sigwalt[121,122] and also subsequently by Ishii[124]. In a later paper, Ishii and coworkers[124] showed that under strict control of the water content the $Al(C_2H_5)_3$ + H_2O system is active for the polymerisation and copolymerisation of alkene sulphides in toluene at 0–50°C. The influence of the ratio of the components in the initial mixture, the polarity of the medium, and the concentrations of the monomer and catalyst on the rate of the process and the molecular weight of the polymer were investigated. It was found that in comparison with pure $Al(C_2H_5)_3$ the $Al(C_2H_5)_3$ + H_2O system is more active for polymerisation over a wide range of component ratios, and maximal activity is observed at the ratio $Al/H_2O = 1$.

On the basis of various kinetic regularities the polymerisation of PS in the presence of the $Al(C_2H_5)_3$ + H_2O system and its copolymerisation with other α-thio-oxides, conclusions were drawn about the cationic nature of the polymeric chain growth at active centres of the



type and about the presence of intensively developing chain transfer reactions at the monomer or sulphur atoms of the polymeric chain but we do not think that the proposed scheme for these reactions is sufficiently clear.

From the standpoint of the stereospecificity of the catalyst used, the diethylzinc–water system proposed in 1958 by Furukawa and coworkers[111,127] for the polymerisation of cyclic oxides is interesting. This system attracted the attention of many investigators and is now being studied intensively. Many papers have been published about the use of various modifiers with the aim of increasing the effectiveness of this system[58-63,67,115,128].

It is stated in several patents[60-63,67] that $Zn(C_2H_5)_2$ and other organometallic compounds of Group II, modified with compounds which contain atoms with an unshared electron pair or proton-donating additions, are effective in the polymerisation of α-oxides and episulphides and their copolymerisation.

Recently Shozo and Teiji[86] thoroughly investigated the $Zn(C_2H_5)_2 + H_2O$ system for the polymerisation of α-oxides and found that the mechanism of its action (cationic or anionic) is connected with the change in the molar ratio of the components, which is reflected in the structure of the hydrolysis products formed, leading to polymerisation. According to recent results[110], obtained by infrared spectroscopy, gas–liquid chromatography, and X-ray diffraction, $C_2H_5(ZnO)_n.Zn(C_2H_5)$ (I), $C_2H_5(ZnO)_nH$ (II), and $HO(ZnO)_nH$ (III), which have a disordered würtzite structure containing a Zn–O–Zn bond, are excitants of the polymerisation of propene oxide, depending on the degree of hydrolysis. Their relative acidity increases in the order: (III) < $Zn(C_2H_5)_2$ < (I) < $Al(C_2H_5)_3$.

The possibility of the use of this catalytic system for the polymerisation of episulphides was first shown in 1963 by Kabayashi and Ishii[70]. The French investigators Machon and Sigwalt[121,122] made a more detailed investigation of the effect of the addition of water on the extent of the conversion and the properties of the polymer obtained in the polymerisation of PS in benzene solution—the catalytic $Zn(C_2H_5)_2/H_2O$ system. It was shown that the system is effective for the excitation of polymerisation over a wide range of ratios $\rho = H_2O/Zn(C_2H_5)_2$ but the crystallinity of poly(propene sulphide), which was estimated from the solubility of the polymer in ethyl methyl ketone, reaches a maximum at $\rho = 1$. On the basis of extremely few experimental results it is difficult to draw any conclusions about the actual mechanism of the system being studied, but a preference was expressed for the anionic nature of the initiation and growth of the polymeric chain independently of the value of ρ.

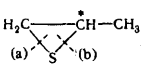
The poly(propene sulphide) obtained is an elastomer with increased rigidity and breaking resistance, its crystallinity is connected with the ratio of the components in the initiating system.

Interesting information about the nature of the active centres in the polymerisation of α-oxides and α-thio-oxides was obtained by Lal[123]. The new systems $Zn(C_2H_5)_2$ + sulphur and $Zn(C_2H_5)_2 + H_2O_2$ were investigated and their action was compared with that of the $Zn(C_2H_5)_2 + H_2O$ system. It was found that sulphur emerges as a cocatalyst and the $Zn(C_2H_5)_2$ + S system effects the heterogeneous polymerisation of α-oxides and α-thio-oxides over a wide range of ratios of the components. During the course of the investigation an effect by the polarity of the medium was not observed and it was shown that all the three systems have similar stereospecificity but the sulphides were polymerised more rapidly than the oxides and had a lower molecular weight. The results obtained led Lal to assume that the effectiveness of the $Zn(C_2H_5)_2$ + S system is associated with the presence of polysulphide bonds. This assumption was confirmed in studying the polymerisation of propene oxide in the presence of model mercaptides of the type: RSZnR, RSZnSR, RS_XZnS_YR, RS_XZnR, and RS_XZnSR (where $x + y = 2-8$). It was shown that the compounds which contain monosulphide bonds of the RSZnR type and the mercaptides obtained *in situ* in the $Zn(C_2H_5)_2$ + S system are ineffective for exciting the polymerisation of α-oxides and thio-oxides. Prolonged ageing of the catalyst $Zn(C_2H_5)_2$ + S (0.5–19 h) facilitates the formation of active polysulphide bonds RS_XZnS_YR, in which the R–S structure also plays a significant part. It is thought that polymerisation proceeds by a coordination mechanism but this problem was not discussed.

To understand and identify the mechanism of polymerisation of α-thio-oxides under the action of various excitants there was great interest in studying the synthesis of optically active polymers from monomers containing asymmetric carbon atoms. It is known that an optically active polymer can be prepared when the polymerisation of the optically active form of the monomer (enantiomer) is carried out, or by using the racemate of an optically active excitant to initiate the polymerisation. Spassky and coworkers[68,75,87,88] used both these possibilities to obtain optically active poly(propene sulphide).

As Machon and Sigwalt showed[121,122], the stereospecific polymerisation of racemic PS allows a high-molecular-weight polymer with up to 50% crystalline phase to be obtained. Spassky[88] thought that the crystallinity of this polymer could be due either to the simultaneous presence of two types of polymer, obtained on the basis of each of the enantiomers, or to the existence of a single polymeric chain consisting of successions of each enantiomer of various lengths. Therefore the preparation of polymers of each antipode should give valuable information about the mechanism of the stereospecific polymerisation of episulphides.

On the other hand, a comparison of the optical activity of the polymers obtained with various catalytic systems allows the presence of an irregularity in the macrochain, due to opening of the ring at the C–S bond at the primary or secondary carbon atom, to be observed. Actually, under the influence of various agents the ring of the optically active PS



can be opened to form a polymer of type (a) (anionic polymerisation) with retention of the configuration at C* and consequently with increase in optical activity, or of type (b) (cationic polymerisation), or of a mixture of types (a) and (b) with loss of or decrease in the optical activity of the polymer. As follows from Spassky's results[68,87], in the polymerisation of *d*- and *l*-propene sulphide under the influence of anionic excitants (sodium, KOH, cadmium tartrate) polymers with increased-optical activity are formed, but under the influence of boron trifluoride–diethyl ether, polymers with reduced optical activity are formed. In this connection there is considerable interest in studying the nature of the action of the $Zn(C_2H_5)_2 + H_2O$ system at various ratios of the initial components. For $Zn(C_2H_5)_2/H_2O = 1:1$ the optical activity is close to that obtained in an anionic system. A reduction in the proportion of water decreases the optical activity, which could be linked with the appearance of a cationic nature in the active centre formed. The system with $Zn(C_2H_5)_2/H_2O = 1:0.5$ is similar in its action to the $Al(C_2H_5)_3/H_2O = 1:0.7$ system and is a cationic excitant[105], but $Zn(C_2H_5)_2/CH_3OH = \frac{1}{2}$ and $Zn(C_2H_5)_2$ + glycol[68] is anionic, which agrees with the results of Inoue and coworkers[128]. It was noted[68,75,87–89] that in the polymerisation of episulphides there is not a complete analogy in the behaviour of the $Zn(C_2H_5)_2/MOH = \frac{1}{2}$ and $Zn(C_2H_5)_2/H_2O = \frac{1}{1}$ systems, since the latter shows a tendency to a cationic nature.

The polymerisation of the racemic *d,l*-propene sulphide in the presence of organolithium and organozinc compounds modified with optically active additions [LiC_4H_9 + LiOR*, $Zn(C_2H_5)_2$ + 2ROH*] was studied by Aliev and Krentsel'.[129,130] In an investigation of the lithium system low-molecular-weight polymers exhibiting a comparatively high optical activity (up to −63.7 deg) were obtained. The polymerisation was accompanied by the release of propene and under certain conditions there was almost complete decomposition of the poly(propene sulphide) into propene and

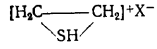
elemental sulphur. The process could also be directed to the production of a polymer with S–S bonds. It was suggested[129] that under the action of a strongly nucleophilic agent polymerisation takes place in three successive directions: (a) desulphidation of the PS and polymerisation, (b) decomposition of the polymer chains with release of propene and formation of oligomeric products with ~S–Li groups at both ends of the chain, (c) oxidation of the oligomers either by elemental sulphur or by lithium polysulphide with the formation of polymers with disulphide bonds.

Another probable mechanism of initiation and chain growth with formation of disulphide bonds has been suggested[130]. The formation of propene and polysulphide bonds in a macromolecule was also observed in a study[41] of the polymerisation of PS in the presence of zinc and cadmium mercaptides, which the investigators attributed to the act of elimination of sulphur in the coordination of S–Zn–S bonds of a polymeric chain with a monomer.

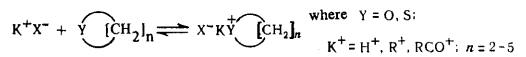
3. Cationic Polymerisation of Alkene Sulphides

The ability of alkene sulphides to polymerise in the presence of excitants of cationic type has been noted repeatedly[8,24,43,49,50]. In 1920 Délépin[8], who had been the first to synthesise episulphides, drew attention to the fact that they are readily polymerised under the influence of dilute mineral acids and acetic acid. In 1960 Dermer showed[24] that boron trifluoride and tetramethylammonium chloride bring about the polymerisation of episulphides in bulk with great velocity, and Boileau[49,50] polymerised PS in the presence of boron trifluoride–diethyl ether and of titanium and aluminium chlorides. However, in these studies only the fact of the formation of a low-molecular-weight polymer was noted and the mechanism of polymerisation under the influence of electrophilic agents was not taken into account.

In 1951 Tarbell and Harnish[131] examined the polymerisation of episulphides in the presence of acidic agents and first suggested the formation of an intermediate sulphonium ion of the type



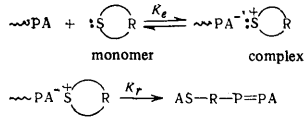
The "onium" mechanism lies at the basis of modern views on the mechanism of cationic polymerisation of heterocycles[132–137]. In the general instance, the initiation of polymerisation is regarded as the interaction of the electron-withdrawing part of the catalyst (Lewis acid) with the unshared electron pair of the heteroatom of the monomer with the formation of a stable onium pair, which is also an active centre of polymerisation:



The capability of the reacting substances to form onium (or sulphonium) ion is linked with the strain and basicity of the heterocycle, and also with the acidity of the catalyst, which ensures that the ionic complex is of sufficient stability.

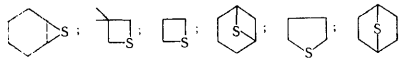
Oddon[138] made a detailed study of the reactivity of three-membered sulphur-containing heterocycles in relation to electrophilic agents; Stille and Empen[25,26] attempted to correlate between the physicochemical parameters of various cyclic sulphides and their capability for polymerisation.

In the first publication[25] the possibility of polymerisation of alkene sulphides with rings of various sizes in the presence of $Al(C_2H_5)_3$ and PF_5 was reported; it was suggested that it proceeds by the usual mechanism:



where PA is the growing polymer and A the electron acceptor.

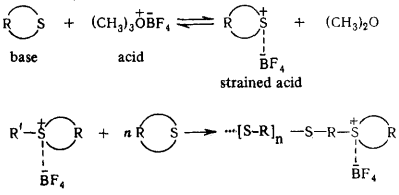
Subsequently[26], by assuming that the polymerisation, at the start of which coordination or complex formation occurs, should be determined both by the basicity of the cyclic sulphide and by its tendency to ring opening, Stille and Empen determined the basicity of six cyclic sulphides:



and investigated their capability for polymerisation under the influence of the systems: (1) $AlR_3 + H_2O$ + epichlorhydrin, (2) PF_5, (3) $BF_3:O(C_2H_5)_2$ + epichlorhydrin, (4) $R_3O:BF_4$.

The basicity was estimated from the shift of the absorption band of the OH group in the infrared spectra of solutions of phenol and sulphides in CCl_4 and also from the heat of complex formation with iodine. The order of basicity found for alkene sulphides with various ring sizes ($5 > 6 > 4 > 3$) differs from that for oxides ($4 > 5 > 6 > 3$) and agrees with other results[100,139–143]. The basicity series for the oxides and thio-oxides are connected with the difference in size of the heteroatoms, the strain of the ring, and the polarisability of the bonds. On comparing the heats of formation of the complex and the heats of polymerisation it was concluded that the conversion of a cyclic sulphide into a polymer is determined not so much by its basicity as by the ring strain.

On considering the mechanism of polymerisation of alkene sulphides under the influence of trialkyloxonium salts we have suggested that, by analogy with the reactions studied by Meerwein[144,145], leading to the formation of trialkylsulphonium salts from trialkyloxonium salts and dialkyl sulphide—in this instance a stable trialkylsulphonium salt is formed, brought about by polymerisation:

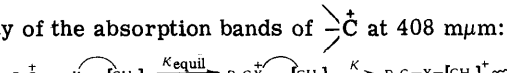


Extremely interesting results dealing with the reactivity of thio-oxides and the stability of sulphonium ions were given by Japanese scientists[146]. They measured the constants of the equilibrium

$$\text{carbonium} \underset{}{\overset{K_{equil}}{\rightleftharpoons}} \text{oxonium and}$$

$$\text{carbonium} \underset{}{\overset{K'_{equil}}{\rightleftharpoons}} \text{sulphonium}$$

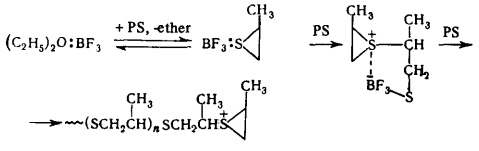
for the reactions of trityl hexachloroantimonate with various cyclic oxides and thio-oxides from the decrease in the intensity of the absorption bands of $\text{>}\overset{+}{\text{C}}\text{<}$ at 408 mμm:



where X = S, O; Y = nucleophile.

It was shown that in every instance the equilibrium of the reaction is shifted to the right and the equilibrium constants (K_{equil}) for the thio-oxides considerably exceed those for the oxides. Sakai and coworkers associate these results with the greater stability of the sulphonium salts. They used K_{equil} and K'_{equil} to calculate the apparent rate constant for the opening of the heterocycle (k) and found that according to reactivity the sulphides can be arranged in the order $4 > 5 > 3$, which agrees with the results on their basicity but not with those on their ability to polymerise ($3 > 4 > 5$). The stability of the sulphonium salts, which depends on their structure and the nature of the counter-ion, determines the temperature range in which they can be used for the excitation of the polymerisation of PS. It has been shown[23] that despite the similar values for the activation energy of the polymerisation of PS in the presence of boron trifluoride–diethyl ether, and of its trialkyloxonium and trialkylsulphonium salts (E_{act} = 18 ± 2, 16 ± 0.5, and 20 ± 0.5 kcal mole^{-1} respectively) in the last instance the polymerisation is effected only above 50°C whereas for the first two inducers polymerisation proceeds effectively from 0° to 20°C.

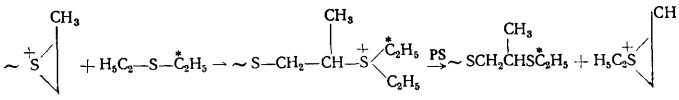
The polymerisation of PS under the influence of a typically cationic inducer, boron trifluoride–diethyl ether, has been studied repeatedly[99,147,148]. In ethyl chloride, nitroethane, or diethyl ether solution at 20°C and monomer concentrations of 3.5–6.4 M and inducer concentrations of 1.5×10^{-3}–9.0×10^{-3} M the polymerisation develops with participation of "living" polymeric chains without an induction period, irreversibly until complete depletion of the monomer, with the formation of a polymer which exhibits relatively broad MWD. The total activation energy of the process in 18 ± 1.5 kcal mole^{-1}. By initiating the polymerisation with seed "living" polymers the investigators showed that the high value of E_{act} is determined mainly by the limiting stage of the opening of the episulphide ring. The overall expression for the initial rate is $v_p = k_p[PS][cat]$, where k_p = 3.35 litre mole^{-1} min^{-1}. It is assumed that growth of the polymeric chain is effected by the stable sulphonium ion, formed according to the scheme:



It was shown[99,147,148] that the polymerisation of PS in the presence of boron trifluoride–diethyl ether is complicated by interchain exchange interaction the contribution of which increases with the degree of conversion. This is proved by the change in the nature of the MWD curves during the polymerisation and after its completion, the decrease in the molecular weight of the polymer during the polymerisation in the presence of dialkylsulphides and the possibility of the preparation of block-copolymers during the polymerisation of ethylene sulphide in a solution of "dead" poly(propene sulphide).

Enikolopyan and coworkers[149,150] developed the theory of interchain exchange interaction by the example of oxygen-containing heterocycles. A similar conversion of macromolecules is now known as a chain transfer reaction with chain breaking (CTB).

By making certain assumptions, a quantitative estimation of the contribution of the CTB in the polymerisation of PS under the influence of boron trifluoride–diethyl ether in the presence of diethyl sulphide (DES) labelled with ^{14}C was made[23,99]. The great stability of the sulphonium ions and the specific structure of the polymeric chain in which the basicity of the heteroatom is close to the interaction of the active centre not only with the monomer but also with the DES modelling the polymeric chain:



The polymerisation was studied at various stages of the conversion and characterised by the ^{14}C content in the polymeric chain. E_{act}CTB was calculated from the change in the rate of reaction of CTB in the temperature range 20–50°C and found to be 15 ± 2 kcal mole^{-1}, which corresponds to published results on the activation energy of thioether exchange[151]. By considering the polymerisation of PS under the action of boron trifluoride–diethyl ether as a "pseudocopolymerisation", in which $k_{DES-DES} = 0$, the relative value of the constant of the CTB reaction as

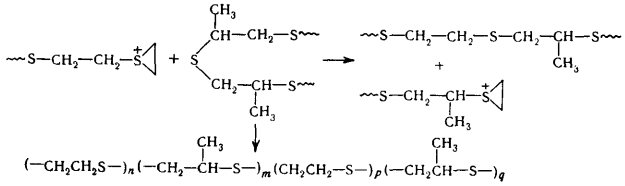
$$\frac{k_{CTB}}{k_{growth}} = [M]/[DES]\frac{\Delta DES}{\Delta M},$$

where [M] and [DES] are the concentrations of the monomer and DES in the initial mixture, and ΔM and ΔDES are the mole fractions of PS and DES in the polymer respectively.

By calculations from the radioactivity of the polymer, obtained at various compositions of the initial mixture,

$$k'_{CTB} = \frac{k_{CTB}}{k_{growth}} = 2 \cdot 10^{-3},$$

which shows the insignificant contribution to the CTB reaction at the stages which do not exceed 10% conversion. The CTB reaction develops more intensively on replacing DES by the already polymerised chain, that is, when there is a considerable increase in the concentration of thioacetal groups[99,147,148,152]. The polymerisation of ES under the influence of a cationic-type inducer in a solution of "dead" poly(propene sulphide) leads to the formation of statistical block-copolymers and was used for the direct proof of the existence of CTB reactions.



The phase composition of the fractions isolated by the method of fractional precipitation and selective extraction was controlled by elemental analysis and calorimetrically. The individual fractions of block-copolymers were investigated by physicochemical methods. The different proportions of crystalline poly(ethylene sulphide) links in the chain of the amorphous poly(propene sulphide) are readily

fixed by X-ray diffraction and are shown by the melting point of the fraction, determined from the thermomechanical curve.

4. Polymerisation of Propene Sulphide under the Influence of Complexes with Charge Transfer Complexes (CTC)

The presence of a lone pair of electrons localised at the sulphur atom in the thiirans suggested that compounds of this class can act as electron-donating partner in interaction with various electron-acceptors, by forming donor–acceptor CTC with development of polymerisation [83-85].

Stotskaya and coworkers showed, by the example of PS, that when it reacts with organic acceptors coloured CTC of the p–π type are formed with a specific absorption band maximum in the ultraviolet range which brings about the polymerisation of PS without the introduction of additional initiating agents. The principal kinetic parameters of the polymerisation of PS in the presence of a weak acceptor of electrons—maleic anhydride (MA) (E_a = 0.5 eV)—and of a strong acceptor—tetranitromethane (TNM) (E_a = 1.2 eV) in polar and non-polar solvents were studied. The polymerisation of PS had specific features which distinguish it from the polymerisation of the thiirans so far studied in the presence of cationic and anionic excitants. Independently of the nature of the acceptor and the polarity of the solvent, the kinetic curves were S-shaped, which the investigators associated with retardation of the initiation. The polymerisation was accompanied by intensively developing chain transfer and breaking reactions. The consumption of the acceptor not only in the formation of CTC but also in other side-processes was also found to be specific. The nature of the acceptor and the polarity of the medium determined the composition of the CTC which appear in the orders of the reaction with respect to the monomer and to the acceptor. Thus in the PS–MA system in a non-polar solvent and in the bulk

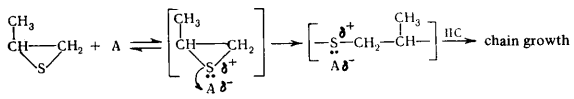
$$v_p = k_1 [PS]^2[MA];$$

in a polar solvent

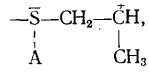
$$v_p = k_p [PS]^2[MA]^2,$$

and when the strong acceptor TNM was used the reaction was of variable order with respect to the acceptor (from 0.5 to 0) and of first order in relation to the monomer. The composition of the donor–acceptor complexes of PS with MA and THM was studied spectrophotometrically and the equilibrium constants for their formation in polar and non-polar media were calculated.

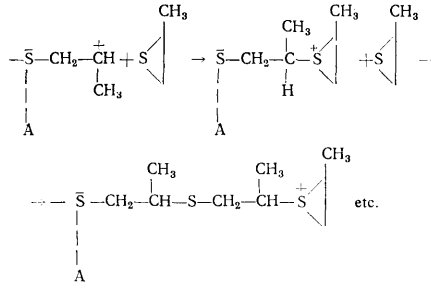
Sitnikova and coworkers [83] first supported a purely coordination mechanism for polymeric chain growth at an active centre formed during the opening of the thiiran ring in the CTC:



Subsequently [85] they concluded that the initiation of polymerisation is effected through a CTC stage, ring opening, and formation of an active centre:



and subsequently the chain growth proceeds by a cationic mechanism with participation of stable sulphonium ions which include the stages of chain transfer and breaking:



Sitnikova and coworkers did not give any experimental facts which confirm the correctness of the proposed mechanism of polymer chain growth.

III. COPOLYMERISATION OF ALKENE SULPHIDES

There is considerable theoretical and practical interest in the rules of copolymerisation of α-thio-oxides with derivatives of the same homological series and with other compounds, and in the properties of the copolymers obtained. The very few papers and patents have shown that the introduction of monosulphide bonds into the main chain of a polymer of another type gives a series of specific valuable properties [153-157]. Two- and three-component copolymers of α-thio-oxides in which one of the monomers has a C=C bond to ensure the possibility of their vulcanisation are of definite practical interest.

Kabayashi and Morivaki [76] obtained such a rubber on the basis of PS and allyloxypropene sulphide in the presence of various cadmium compounds. Thanks to the presence of thioether groups the rubber had good acid resistance and antioxidants were not needed in the vulcanisation usual for rubber.

Adamek and coworkers [72] used a three-component system of ethylene sulphide, PS, and allyloxymethylthiiran, and by employing zinc and cadmium carbonates as catalysts also obtained a vulcanising rubber. In comparison with the rubbers obtained by Kabayashi, the three-component copolymer had increased mechanical strength associated with the presence of a crystalline phase due to the ethylene sulphide links. The copolymer is stable to ozonation, certain chemical reagents, and over a wide range of temperatures it exhibits physicomechanical properties close to standard butadiene–styrene rubber. One of the features of the ternary copolymer is the rapidity of the vulcanisation (thrice as rapid as for the copolymer based on propene oxide). The capability of thiirans to give "living" polymeric chains has been used by many investigators for the production of block-copolymers. Thus Pstrosky [158] obtained block copolymers of ethylene sulphide with styrene and 4-vinylpyridine but Robert and Pearce [159] prepared block-copolymers of ethylene and propene sulphides with methyl methacrylate, styrene, and α-methylstyrene. French scientists obtained block copolymers of dienes with episulphides [153, 154].

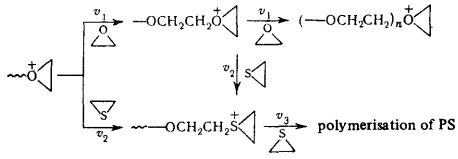
In every instance for the preparation of block copolymers in the initiation of polymerisation of episulphides by "living" polymers obtained in the anionic polymerisation of vinyl monomers or of dienes the quantitative conversion of the $-C^-$ active centre into $-S^-$ was used.

The relative reactivity of thiirans in anionic and cationic copolymerisation was studied by Bualo [190] and

Spassky[27]. It was found that the basicity of thiiran does not affect its activity during anionic copolymerisation[160]. On the basis of a comparison of the constants for the copolymerisation of PS and cyclohexene sulphide—initiating systems of boron trifluoride–diethyl ether and of $Zn(C_2H_5)_2 + H_2O$ at a component ratio of 1 : 1—Spassky drew conclusions about the common mechanism of action of these catalytic systems and the basicity of the monomers determined their relative reactivity[27].

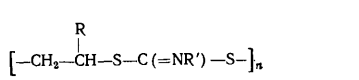
Copolymers of α-oxides with α-thio-oxides have been described in the patent literature[61,62,155-157,161]. Copolymerisation is effected under the influence of alkali metal hydroxides or of modified organometallic compounds at 25–175°C. The polymers formed exhibit high resistance to oxidation and are recommended for practical use as dielectrics and additions to lubricating oils and consistent lubricants. Copolymers of trioxan with a small quantity of thiiran obtained from boron trifluoride–diethyl ether[56,162] exhibit a thermal stability greater than that of homopolymers or other copolymers of trioxan.

The possibility of the copolymerisation of thiirans with their oxygen analogues under the influence of inducers of the cationic type has been studied[163,164]. It was shown that in the presence of boron trifluoride–diethyl ether and trialkyloxonium salts over a wide range of PS and propene oxide, or epichlorhydrin concentrations polymers enriched in thiiran are formed. Having studied certain kinetic regularities of the process and the composition of the polymers formed, the investigators showed that the irreversible and quantitative conversion of the oxonium ion into the stable sulphonium ion rules out the possibility of the formation of a statistical copolymer of thiiran with oxiran, and in this instance only block copolymers or their mixtures with a homopolymer of thio-oxide could be obtained. The composition and structure of the polymer are determined by the ratio of the rates v_1, v_2, and v_3 of the processes which occur:



The irreversible change oxonium → sulphonium was used to prepare block-copolymers in the initiation of the polymerisation of thio-oxides by "living" polymers of polyoxides. On taking into account the intensely developing interchain exchange reactions which are characteristic of cationic polymerisation of heterocyclic compounds, we thought it possible to obtain[163] block-copolymers of a specified composition, but it was difficult to calculate for the formation of copolymers with sections of polyoxide and polythio-oxide of definite dimensions.

There have recently been studies of the copolymerisation of thio-oxides with carbon disulphide[165] and isothiocyanates[166]. Under the action of tertiary amines first an oligomeric ethylene trithiocarbonate is obtained, then low-molecular-weight crystalline copolymers with the structure:

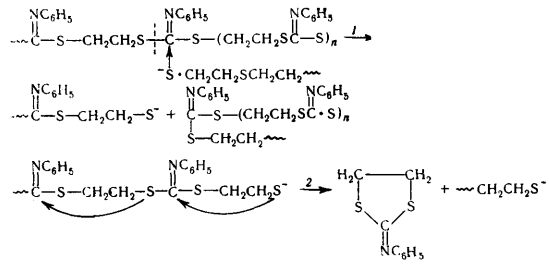


These investigations have progressed considerably[23,167-172]. In studying the copolymerisation of thio-oxides with isothiocyanates under the influence of butyllithium or the sodium–naphthalene complex in THF solution it was found that the process proceeds by a "living" chain mechanism with the formation of high-molecular-weight products exhibiting increased resistance to radiation. Some of the rules for the process were investigated by the example of the copolymerisation of ethylene sulphide with phenyl isothiocyanate. The isothiocyanate, which is active in relation to the inducer and to the $-CH_2CH_2S^-$ anion, reacts at a high rate with butyllithium, forming the anion of low activity $-C(=NR)S^-$, which is incapable of breaking the C=S bond of the isothiocyanate, but breaks the α-thio-oxide ring. Such selective interaction of the monomer with anions of different activity leads to the preparation of a copolymer of strictly alternating structure. In this process the relative reactivity of the phenyl isothiocyanate is considerably greater than that for alkyl isothiocyanates[170].

At equimolecular ratios of the reactants or with an excess of isothiocyanate a copolymer is formed in quantitative yield. An excess of ethylene sulphide (which is capable of homopolymerisation) does not lead to the production of the block-copolymer

$$[-SCH_2CH_2SC(=NR)S-]_n \cdot [-SCH_2CH_2]_m,$$

of calculated composition; the process is complicated by secondary phenomena arising after the disappearance of isothiocyanate from the system. The active polymeric anion $\sim CH_2CH_2SCH_2CH_2S^-$, by acting on the chain of the copolymer, brings about its breakdown to cyclic 2-phenylimino-1,3-dithiolane:



Finally, in the excess of ethylene sulphide there is complete breakdown of the copolymer that has been formed into cyclic dithiolane and the quantitative formation of the homopolymer of ES. In the copolymerisation of equimolecular quantities of phenyl isothiocyanate and PS it was shown that at 20°C even at different stages of the conversion the growth of the chain of the copolymer is accompanied by the formation of 2-phenylimino-4-methyl-1,3-dithiolan and above 65°C the process is shifted completely to the side of formation of the less strained cyclic dimer. Carrying out the copolymerisation under milder conditions in the presence of hexamethylphosphortriamide leads to a minimum in the decomposition of the copolymer[171].

From the published results discussed above the polymerisation and copolymerisation of thio-oxides under the influence of various catalytic systems has attracted great attention. In the most recent publications special sections are devoted to these problems[57,90]. There have been communications dealing with the possibility of the practical application of polymeric materials based on poly(alkene sulphides).[174-176] This all provides a basis for suggesting the wide use of polymers based on alkene sulphides in the not too distant future.

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