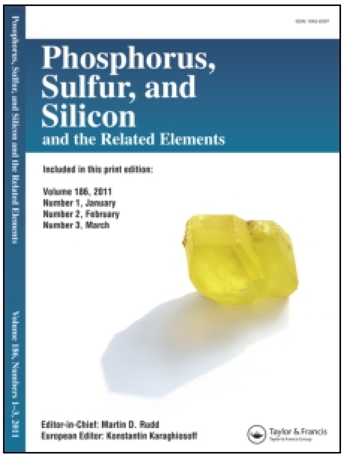

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POLYMERIZATION AND COPOLYMERIZATION OF ELEMENTAL SULFUR

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POLYMERIZATION AND COPOLYMERIZATION OF ELEMENTAL SULFUR

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Abstract Anionic copolymerization of elemental sulfur (S_8) with cyclic monosulfides (thiiranes) is shortly reviewed. More recent work on homopolymerization of cyclic trisulfides (1,2,3-trithiolanes) and their copolymerization with S_8 is discussed in more detail. Anionic homopolymerization of cyclic trisulfides is a living, highly reversible process. Repeating units of the resulting polymers have exclusively alkylene trisulfides structure. No elemental sulfur is eliminated in polymerization. The thermodynamic parameters of equilibrium have been determined for both homopolymerization of norbornene trisulfide (NS_3) and endo-dicyclopentadiene trisulfide (DS_3): $\Delta H^o_{ss} = -5.8\pm0.7$ and -6.6 ± 0.6 kJ/mol, $\Delta S^o_{ss} = -31.4\pm2.3$ and -29.3 ± 2.1 J/mol·K (first values for NS_3). Spectroscopic data (Laser Raman and NMR spectra) clearly indicate that in the copolymerization of elemental sulfur with cyclic trisulfides copolymers are formed. The ultimate number of sulfur atoms in the polysulfide units approaches nine (like in the copolymerization of thiiranes with S_8). Copolymers are high molecular elastomers, in contrast to the rigid, glassy homopolymers of NS_3 and DS_3.

INTRODUCTION

Thermal homopolymerization of elemental sulfur is a well known process. Cyclooctasulfur, the most thermodynamically stable form of elemental sulfur under normal conditions, is converted almost entirely into the linear polymeric polysulfur.[1,2] Thermodynamics of this conversion was studied mostly by Tobolsky and Eisenberg and described quantitatively in therms of initiation and propagation reactions. Both are reversible. Polysulfur (S_n) is thermodynamically stable only above 159°C.[2,3]

Polysulfur eventually gives highly crystalline, insoluble product melting only with depolymerization to S_8.[2,4] Attempts to make polysulfur related products more tractable by using the free-radical copolymerization, mostly studied in the fifties, have been unsuccessfull.[5-7]

The reasons of this failure were discussed recently in our review papers.[8,9] Thus, in copolymerization with vinyl monomers there are two kinds of macroradicals: $\ldots\text{-C}^{*}R_2$ and $\ldots\text{-S}^{*}_{j}$, where $1<j<8$. The former macroradical reacts much faster with S_8 than with a parent vinyl monomer, the latter macroradicals recombine faster than the addition of vinyl monomer takes place. These conditions result shortly in the relatively low yield of the low molecular weight material.[6]

ANIONIC COPOLYMERIZATION OF SULFUR WITH THIIRANES

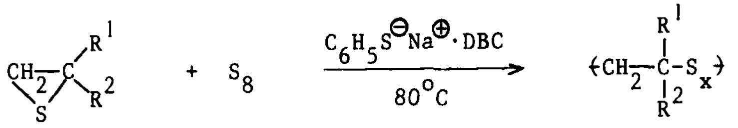
Copolymerization of S_8 with thiiranes, leading to the high molecular weight, stable, crystalline or amorphous copolymer (depending on thiirane used) was described for the first time by the present authors.[10] The sulfur content was as high as 85% (e.g. in copolymer of S_8 with methylthiirane).

In contrast to the crystalline polysulfur, a number of these copolymers, even with high sulfur content, are soluble in organic solvents.

Copolymerization with thiiranes has already been reviewed at one of the IUPAC Symposia;[8] therefore only a brief account of this work will be given in this paper.

Conditions of copolymerization

Although anionic copolymerization of S_8 could be induced by a number of initiators, crowned sodium thiophenolate was used almost exclusively. Addition of crown ether (18-dibenzo-crown-6, DBC) was necessary to solubilize initiator in the polymerization mixtures, containing benzene, toluene or molten sulfur as solvents. Thiirane, 2-methylthiirane, and 2,2-dimethylthiirane were used as comonomers:



(1)

$R^1 = \text{H},\ R^2 = \text{CH}_3$ where $x \leqslant 9$

or $R^1 = R^2 = \text{H}$ or CH_3 $\overline{M}n(\text{GPC}) \leqslant 5\cdot 10^4$

According to the ^1H, ^{13}C-NMR and Raman spectra of the reaction mixtures, as well as of the isolated and purified copolymers, thes are linear poly(alkylene polysulfides), as shown in Eq. (1).[11-13]

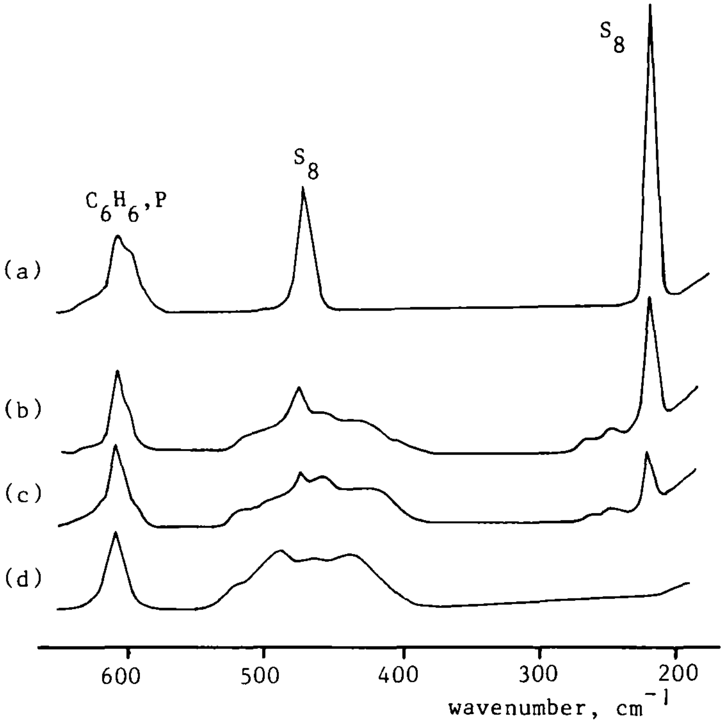


FIGURE 1 Raman spectra (Laser $Ar^{\oplus}$, 20°C) of 2-methylthiirane (P) - S_8 reaction mixtures in benzene as solvent
(a) at the start of copolymerization, t = 0
(b) and (c) during copolymerization, t = 30 and 80 min respectively
(d) spectrum of P - S_8 copolymer
Conditions of copolymerization:
$[C_6H_5S^{\ominus}Na^{\oplus}\cdot DBC]_o = 10^{-3}$ mol/l, $[S_8]_o = 0.25$ mol/l, $[P]_o = 1.0$ mol/l, t = 80°C

Particularly useful are the Raman spectra. Figure 1, taken from Ref. 13, shows the gradual disappearance, during copolymerization, of the sharp band at 217 cm^{-1}, due to the cyclo-S_8.

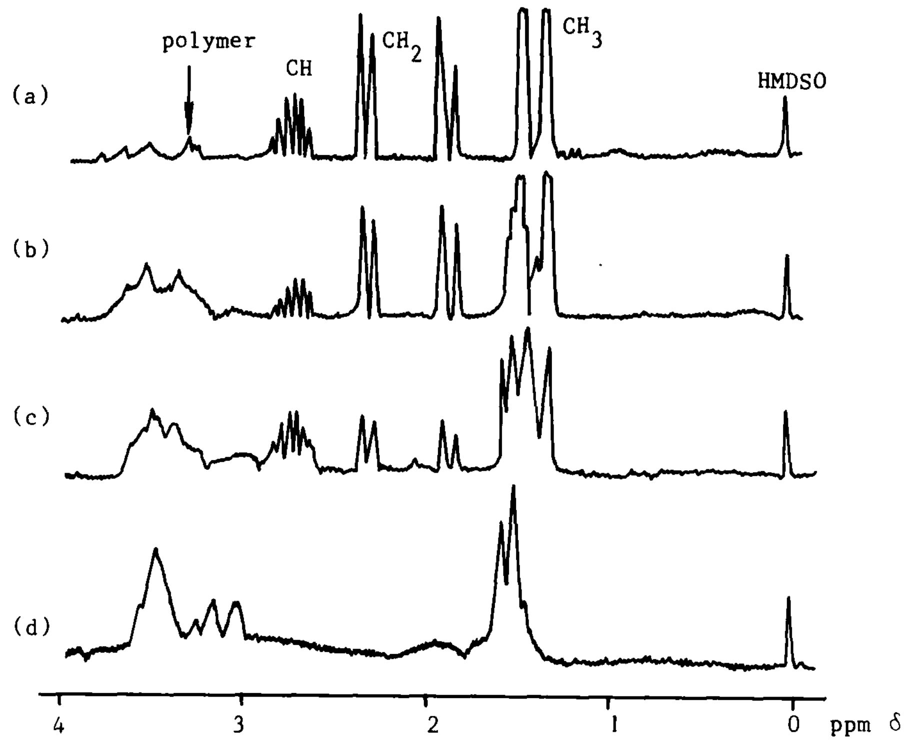


FIGURE 2 ^{1}H NMR spectra (60 MHz, 35°C) of P - S_8 reaction mixtures. Other conditions as in Figure 1.

^{1}H-NMR spectra allow to observe conversion of thiiranes. Thus, in Figure 2, taken from the same work, the evolution of the 2-methylthiirane spectrum clearly indicates rupture of the ring and formation of the linear polysulfides (note the CH_2 region[14]).

Both the Raman and NMR spectra allowed to establish: the higher the proportion of S_8 in the feed (the comonomers mixture) the reacher in sulfur is the resulting copolymer. Increasing of copolymerization temperature has virtually the same effect.[15] When copolymerization is conducted below the floor temperature of sulfur homopolymerization, then the limit of number of sulfur atoms in the bridges linking alkylene units approaches the value of 9. This is because the rate of depropagation to S_8 from the longer units becomes higher than the rate of S_8 addition.

Kinetics of Copolymerization

The kinetic scheme of S_8 copolymerization was formulated and solved.[12] In this scheme addition of thiirane (P) to the growing anions is considered to be irreversible, due to the high thiirane ring strain, whereas addition of S_8 is a reversible process.

This scheme is shown below:

$$\begin{array}{lcllcl} P^* & + & P & \xrightarrow{k_{pp}} & P^* & \\ P^* & + & S_8 & \underset{k_{-ps}}{\overset{k_{ps}}{\rightleftarrows}} & S^* & \\ S^* & + & P & \xrightarrow{k_{sp}} & P^* & \\ S^* & + & S_8 & \underset{k_{-ss}}{\overset{k_{ss}}{\rightleftarrows}} & S^* & (k_{-ss} \gg k_{ss}) \end{array} \tag{2}$$

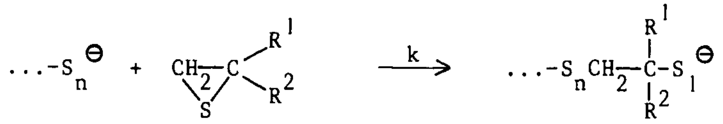
where: $P^* = ...\text{-}CH_2CH(CH_3)S_1^{\ominus}$, $S^* = ...\text{-}CH_2CH(CH_3)S_9^{\ominus}$

Although the fast scrambling reactions, e.g.:

$$\begin{array}{l} ...\text{-}CH_2C(R^1R^2)\text{-}S_9\text{-}CH_2C(R^1R^2)\text{-}... + ...\text{-}CH_2C(R^1R^2)S^{\ominus} \rightleftarrows \\ \rightleftarrows ..\text{-}CH_2C(R^1R^2)\text{-}S_{10-n}\text{-}CH_2C(R^1R^2)\text{-}... + ...\text{-}CH_2(R^1R^2)S_n^{\ominus} \end{array} \tag{3}$$

lead to a certain distribution of the number of S atoms in the polysulfanide anions, Scheme 2 assuming presence only of $...\text{-}S_1^{\ominus}$ and $...\text{-}S_9^{\ominus}$ anions should be valid at least at the very beginning of copolymerization. After analytically solving differential equations following from Scheme 2, we have determined k_{ps}/k_{pp} and k_{sp}/k_{-ps} reactivity ratios.[12] Thus, the thiolate anion $...\text{-}S_1^{\ominus}$ (shown as P^* in Scheme 2) reacts with S_8 almost ten times faster than with 2-methylthiirane ($k_{ps}/k_{pp} \sim 10$). The $...\text{-}S_9^{\ominus}$ anion (S^*), on the other hand, reacts approx. one hundred times faster with P (when $[P] = 1$ mol/l) than it depropagates ($k_{sp}/k_{-ps} \sim 10^2$) (data for 80°C, in C_6H_6 solvent)

It follows also from the kinetic studies that the reactivity of the polysulfanide anion ($...\text{-}CH_2CH(CH_3)S_n^{\ominus}$) falls down with increasing n. For instance, the rate constant of addition of methylthiirane to $...\text{-}S_n^{\ominus}$ anion decreases from 5.5 l/mol·s for n=1 to 0.17 mol/l·s for $\bar{x} \geqslant 4$ (C_6H_6 solvent, 80°C).[13] This could be expected, since the $...\text{-}S_n^{\ominus}$ anion stabilizes by the preceding sulfide sulfur atoms.[16] Moreover, it has been established, that the reactivity of thiiranes with $...\text{-}S_n^{\ominus}$ anions depends on the extent of thiirane substitution. The corresponding relative ratios of reactivities, expressed by the ratio of rate constants:[13]



$$...\text{-}S_n^{\ominus} + CH_2\text{—}C(R^1)(R^2)\text{—}S \xrightarrow{k} ...\text{-}S_nCH_2\text{—}C(R^1)(R^2)\text{-}S_1^{\ominus} \qquad (4)$$

is as follows:

$$k(R^1{=}R^2{=}H) : k(R^1{=}H,\ R^2{=}CH_3) : k(R^1{=}R^2{=}CH_3) = 1:0.5:0.15$$

This is very close to what has been observed in the copolymerization of the corresponding thiiranes.[17]

Low Molecular Weight Cyclic Intermediates

In the anionic copolymerization of S_8, apart from the linear polymeric polysulfides, formation of the transient cyclic, low molecular weight polysulfides was detected by the glc/ms method and confirmed later by ^1H NMR and Laser Raman spectroscopies.[11,13] This was particularly evident in the copolymerization with 2,2-dimethyl thiirane (IBS). In the mixture of cyclic isobutylene polysulfides (IBS_n) concentrations of tri-, tetra- and pentasulfides (n=3,4,5) were predominant. The distribution of n depends on the $[S_8]_o/[IBS]_o$ in the feed.

In Figure 3 (data taken from Ref. 13) the concentration changes of IBS_3 are compared with consumption of both S_8 and IBS and with polymer formation. At the beginning of polymerization mostly IBS_3 is formed. Its maximum concentration is reached simultaneously with the maximum conversion degree of S_8. Then IBS_3 vanishes almost completely with a progress of copolymerization.

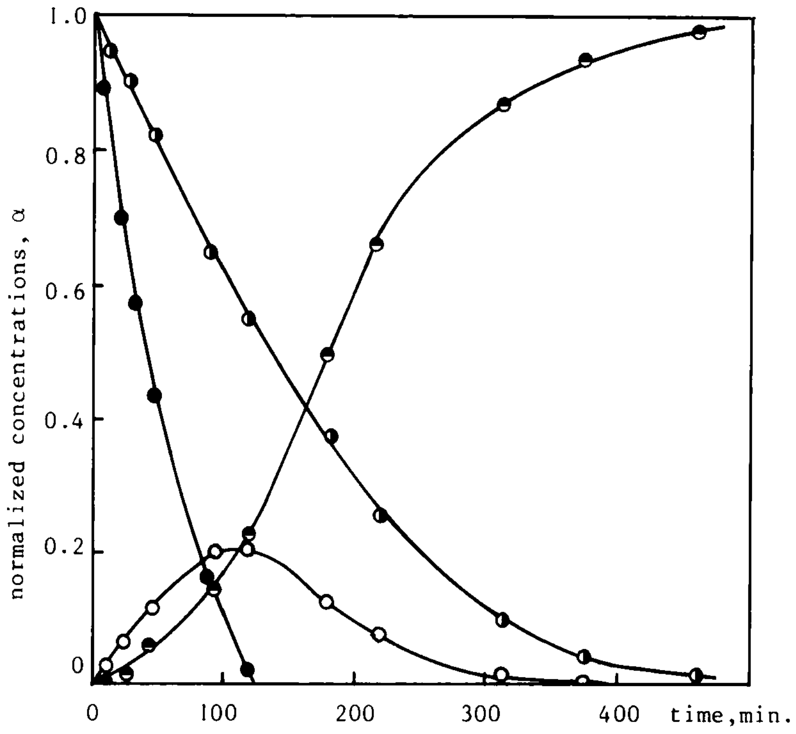
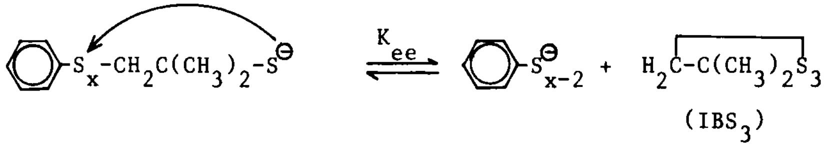


FIGURE 3 Kinetics of copolymerization of 2,2-dimethyl thiirane (IBS) with S_8 in C_6H_6 solution at 80°C. Conditions: $[C_6H_5S^{\ominus},Na^{\oplus}\cdot DBC]_o = 10^{-3}$ mol/l, $[S_8]_o = 0.25$ mol/l, $[IBS]_o = 1$ mol/l. α = (●)$([S_8]-[S_8]_{eq})/([S_8]_o-[S_8]_{eq})$, (◑) $[IBS]/[IBS]_o$, (○) $[IBS_3]/[IBS]_o$, (◓) $[IBS]_{cop}/[IBS]_o$. Where: $[S_8]_{eq}$: concentration of S_8 at equilibrium, when copolymerization is completed; $[IBS]_{cop}$: concentration of copolymer expressed in IBS repeating units.

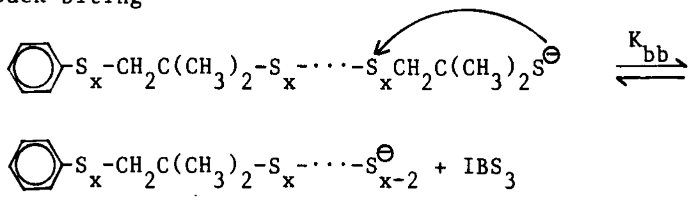
Formation of IBS_3 can be visualised as follows

a) by end-to-end biting



(5)

b) by back-biting



(6)

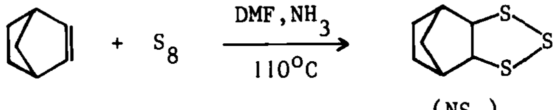
($C_6H_5-S^{\ominus}Na^{\oplus}$·DBC was used as an initiator in these experiments)

The observed changes of IBS_3 are due to the competition between its formation and consumption. At the beginning of copolymerization, for large x values, equilibria (5) and (6) are shifted practically into the right hand side . The IBS_3 formed does not homopolymerize, its concentration is below the equilibrium concentration. When the concentration of S_8 decreases the polysulfur bridges become shorter and equilibria (5) and (6) shift gradually into the opposite side.

However, it can not be excluded that the decreasing rate of IBS_3 formation is also due to the replacing of the end-to-end biting by the back-biting when the copolymer chains are becoming longer. End-to-end biting may proceed more efficiently ($K_{ee}>K_{bb}$) because the reformed arylpolysulfanide anion is more stable in comparison with alkylpolysulfanide anion.

POLYMERIZATION AND COPOLYMERIZATION OF S_8 WITH CYCLIC TRISULFIDES

The described in the previous paragraph formation and polymerization of transient isobutylene polysulfides turned our attention to this class of compounds. Polymerizations of some 1,2-dithia- and 1,2,3--trithiacycloalkanes have been known for some time.[9] However, especially interesting are these cyclic trisulfides that can be prepared directly from S_8 and an olefin (thiiranes cannot be synthesized this way). Thus, we prepared norbornene and dicyclopentadienetrisulfides by the known procedures, involving reactions of S_8 with the corresponding olefins in DMF solvent in the presence of NH_3,[18,19] e.g.:



(7)

(NS_3)

Anionic Homopolymerization of 1,2,3-trithiolanes

Anionic polymerization of both NS_3 and dicyclopentadiene trisulfides (DS_3) is a living process.[20,21] Elemental analysis gave the polymer composition identical to this of the starting monomers. Moreover, in the Raman spectra, of the polymer-monomer mixtures, the band at $217 cm^{-1}$, characteristic for S_8, is absent. Therefore, polymerization proceeds without elimination of the elemental sulfur. Initiated with crowned sodium thiophenolate in bulk or in solution (C_6H_6 or $C_6H_5CH_3$ were used as solvent) polymerization goes to the living polymer-monomer equilibrium. At this stage polymerization was stopped by addition of allylbromide. The equilibrium monomer concentration was determined by several methods (glc, gravimetry, dilatometry, and Raman spectroscopy).

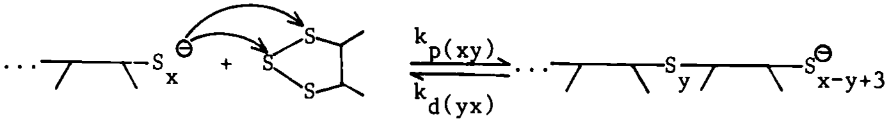
The living nature of NS_3 and DS_3 homopolymerizations has been established in two ways. The polymerization-depolymerization-repolymerization cycles were observed directly by dilatometry; on the other hand, the average molecular masses determined at equilibrium are equal (cf. Table I) to the calculated ones, assuming that every macromolecule is produced by one initiator, i.e. $\overline{Mn} = ([\text{monomer}]_0-[\text{monomer}]_{eq})\cdot\text{M.W.}/[\text{initiator}]_0$, where M.W. is the molecular mass of monomer and $[\text{monomer}]_{eq}$ is the concentration of monomer at equilibrium.

TABLE I Polymerization of norbornene trisulfide and dicyclopentadiene trisulfide. Comparison of $\overline{Mn}$ calculated and $\overline{Mn}$ measured (at 25°C).[20,21]

Monomer [M]	$10^2\cdot[\text{initiator}]_0$ mol/l	$[M]_0$ mol/l	$[M]_{eq}$ mol/l	solvent	$\overline{Mn}$ calcd	$\overline{Mn}$ found
NS_3	0.75	5.85	2.50	C_6H_6	87500	97700
NS_3	1.19	7.03	3.7	$C_6H_5CH_3$	52760	53230
DS_3	0.52	3.9	2.3	$C_6H_5CH_3$	70000	75120
DS_3	1.50	3.8	2.15	C_6H_5	25000	32600

Thermodynamics of NS_3 and DS_3 Homopolymerization

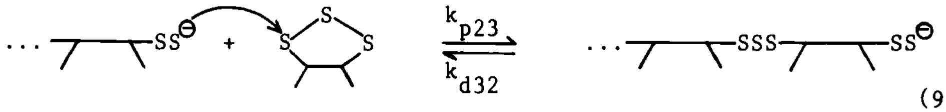
The analysis of the polymerizing mixtures for both monomers revealed that besides the polymer only monomer was present. The living polymer-monomer equilibrium for either NS_3 or DS_3 can be formally presented as follows:



(8)

There are four possible cases related to the site of attack in the ring: x=1, y=2; x=1, y=3; x=2, y=3; and x=2, y=4 (we assume that ring opening follows exclusively the thiophilic attack). Thus, the propagation (k_{pxy}) and depropagation (k_{dyx}) rate constants describe the corresponding equilibrium.

The exclusive formation of NS_3 as the depropagation product has, however, some mechanistic implications, narrowing the number of possible individual equilibria (thus, further restricting the set of the x y numbers). Since ...-$SS^{\ominus}$ anion is more stable than ...-$S^{\ominus}$ anion and since we describe the equilibrium, then even if the attack on the central S atom in the cycle is faster (with formation ...-$S^{\ominus}$ anion), the further fast reshuffling should eventually lead to the exclusive equilibrium:



(9)

This conclusion can be additionally supported by the fact that using end-capping method, based on the reaction of anionic active centers with diphenylchlorophosphate,[22] we have observed in the ^{31}P NMR spectra only the products of polysulfanide anions (...-$S_x^{\ominus}$, $x \geqslant 2$) addition.[23]

Then, the ΔH^{o}_{ss} and ΔS^{o}_{ss} described below are related to the chemical change given by Eq. (9). Thus, at equilibrium:

$$k_{p23}[S_2^{\ominus}][NS_3]_{eq} = k_{d32}[S_2^{\ominus}] \qquad (10)$$

remembering that $K_{eq} = k_{p23}/k_{d32}$ we have

$$K_{eq} = 1/[NS_3]_{eq} \qquad (11)$$

(the same is true for DS_3)

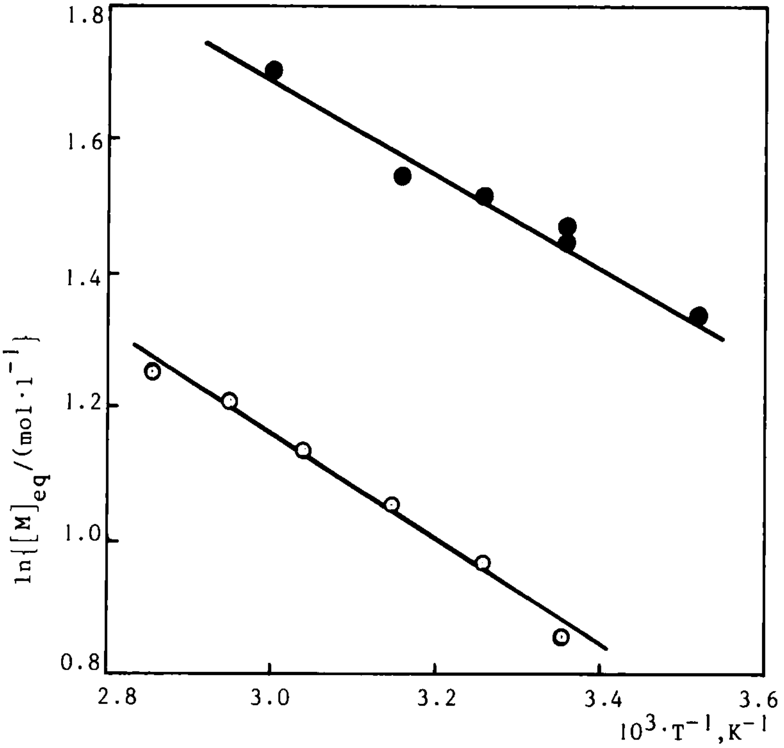


FIGURE 4 Plots of the equilibrium concentrations of NS_3 (●) and DS_3 (○) versus the reciprocal of the absolute temperature. Conditions of polymerization: $[C_6H_5S^{\ominus},Na^{\oplus}.DBC]_o = 10^{-2}$ mol/l, $[NS_3]_o = 6.0$ mol/l $[DS_3]_o = 3.85$ mol/l, toluene as solvent

The dependence of the equilibrium monomer concentration (determined as discussed above) on the reciprocal of the absolute temperature allowed to determine the thermodynamic parameters of polymerization (Figure 4 and Table II).

$$\ln[NS]_{eq} = \frac{\Delta H^o_{ss}}{RT} - \frac{\Delta S^o_{ss}}{R} \qquad (12)$$

In the temperature range of 60°C the equilibrium monomer concentration $[NS]_{eq}$ changes from 3.3 mol/l at 10°C to 6 mol/l at 70°C (70°C is a ceiling temperature, for polymerization in the bulk it is higher because of higher $[NS_3]_o$, cf. Table II).

TABLE II Termodynamic parameters for the polymerizations of NS_3 and DS_3.

Monomer	NS_3	DS_3
ΔH^o_{ss}, kJ/mol	-5.8±0.7	-6.6±0.6
ΔS^o_{ss}, J/mol·K	-31.4±2.3	-29.3±2.1
T_c[a), K	374	440

a) Calculated for polymerization in the bulk, assuming independence of the equilibrium monomer concentration from the starting monomer concentration

According to expectations, the thermodynamic polymerization parameters are close to each other for NS_3 and DS_3. The ring strain is relatively low, whereas for the five-membered disulfide (1,2-dithiolane), it is equal to -25.1 kJ/mol.[24] On the other hand, the five membered monosulfide, tetrahydrothiophene is known to be strainless.

PolyNS_3 and polyDS_3 are amorphous, rather brittle solid materials. For example, for polyNS_3 T_g = 352 K, T_m = 415 K.[25]

Anionic Copolymerization of NS_3 with S_8

Anionic copolymerization of S_8 with NS_3 or DS_3, was conducted in the same way as homopolymerization of trisulfides. In contrast to the brittle homopolymers, the copolymers are rather elastomeric, with much lower solubility (copolymers with higher sulfur content are soluble only in CS_2 or CH_2Br_2) like copolymers of methylthiirane.

The total content of S in copolymers depends on the ratio $[S_8]_o$/ /[comonomer]$_o$ in the feed, as it has been described in the previous paragraphs for thiiranes. Some data are given in Table III.

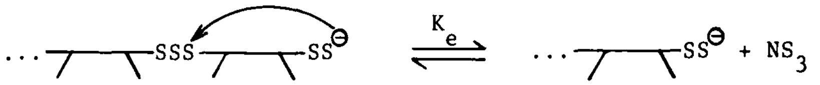
At 25°C S_8 is unable to homopolymerize. However, it is known, that in a system, when one of the comonomers does not homopolymerize, the extent of conversion of this monomer into the polymeric unit increases with increasing of the proportion of the homopolymerizable monomer in the feed.[26,27] Data given in Table III are in agreement with this (intuitively obvious) prediction of the theory.

TABLE III Dependence of the average length of the polysulfide units ($\overline{X}$: "sulfur rank") on the copolymerization conditions (NS_3, bulk, 25°C, $[C_6H_5S^{\ominus},Na^{\oplus}]\cdot DBC_0 = 10^{-2}$ mol/l.

$\dfrac{8[S_8]_0}{8[S_8]_0+[NS_3]_0}$	$8[S_8]_0$	$[NS_3]_0$	$8[S_8]_{eq}$	$[NS_3]_{eq}$	$\overline{X}$ a)
	mol/l				
0	0	7.0	0	3.70	3.0
0.50	6.3	6.3	1.7	3.15	4.5
0.67	11.5	5.7	3.6	3.30	6.2
0.75	15.8	5.3	6.8	3.15	7.2
0.80	19.6	4.8	11.4	3.20	8.0
0.83	22.4	4.5	15.5	3.20	8.4

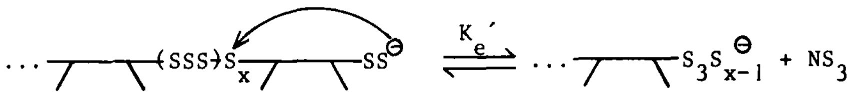
a) $\overline{X}$ determined from analytical data

On the other hand, the equilibrium concentration of NS_3 does not change and equals 3.1-3.7 mol/l. Usually, the equilibrium monomer concentration should decrease with increasing concentration of the comonomer in the feed, because of increasing the population of heterodyads. However, copolymerization of cyclic sulfides with S_8 is very particular in a sense, that the rate of back-biting within a last heterodyad is not decreased in comparison with a homodyad. This is illustrated below; depropagation within a homodyad:



(13)

and depropagation within a heterodyad:



(14)

Since the rate of addition of NS_3 to the $-S_1^{\ominus}$, preceded by a larger number of S atoms, may also decrease, then K_e' can be comparable to K_e. The net effect is that $[NS_3]_e$ is independent on the feed composition.

Laser Raman (LRS) and ^{1}H-NMR Spectra of Polymerizing Mixtures and Copolymers of NS_3 (or DS_3) with S_8

The LRS of the mixture of comonomers, S_8 with NS_3, at the beginning of copolymerization (a) and at equilibrium (b) is shown in Figure 5. The analysis of these spectra is given in Ref. 28. At equilibrium the characteristic line for S_8 at 217 cm^{-1} decreased and a new band, at 240 cm^{-1}, almost absent at the beginning of copolymerization, sharply increases. Some other new bands appear, namely at 170, 300, and 355 cm^{-1}. There is also a multiband new region between 400 and 500 cm^{-1}. In the LRS of the copolymer at equilibrium, the polysulfide bands between 400 and 500 cm^{-1} dominate.

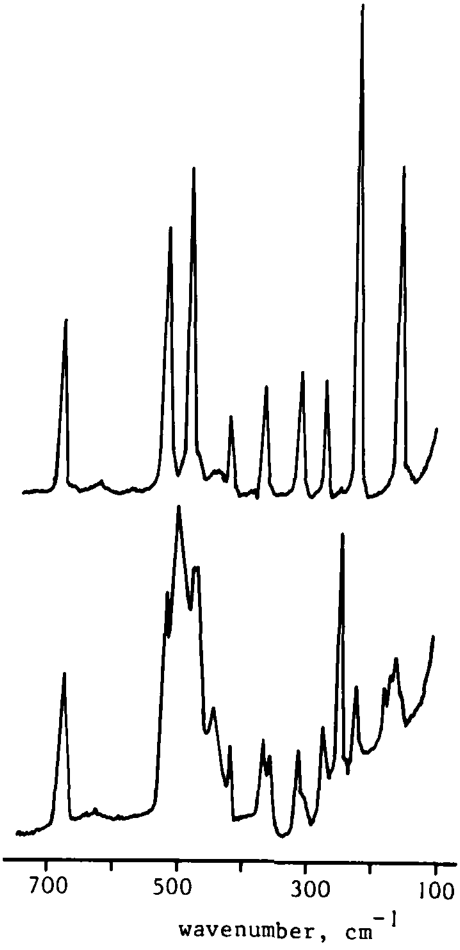


Figure 5

Raman Spectra (laser He-Ne, 25°C) of (a) mixture of NS_3 and S_8 comonomers, (b) polymerization mixture at equilibrium.

Conditions of copolymerization $[C_6H_5S^\ominus, Na^\oplus \cdot DBC]_o = 10^{-2}$ mol/l $8[S_8]_o = 6.3$ mol/l, $[NS_3]_o = 6.3$ mol/l.

^{1}H-NMR spectra of polyNS$_3$ and copolymers of NS$_3$ with S$_8$ change gradually, with increasing the sulfur rank. Lines typical for polyNS$_3$ disappear and new lines appear; however, the quantitative analysis (i.e. determination of the proportions of repeating units with x=3,4.. etc.)has not yet been possible. This is in contrast to the copolymerization of 2,2-dimethylthirane with S$_8$, where in ^{1}H-NMR the chemical shifts of protons in methylene groups $-CH_2-S_x^-$ to S$_1$, S$_2$, S$_3$, and S$_4$, give well resolved, separate singlets,even at 60 MHz.[11,13]

CONCLUSIONS

This paper is summarizing briefly our earlier work on copolymerization of thiiranes, already reviewed at the IUPAC Symposium in 1980,[8] and more extensively our recent work on homo- and copolymerization of cyclic trisulfides with S$_8$. In both processes anionic polymerization was applied, and high molecular weight ($\bar{M}n$ up to 10^5), amorphous polymers were obtained in the living processes.

These copolymerizations became possible since it has been understood that the major factors allowing copolymerization to proceed are: similar reactivities of both growing species and proper interplay of the kinetic and thermodynamic factors. The rate and equilibrium constants have been determined.

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