ANIONIC COPOLYMERIZATION OF ELEMENTAL SULFUR

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Abstract - The radical homo- and copolymerization of ele-
mental sulfur has been reviewed. Reasons of inability of ele-
mental sulfur to copolymerize by radical mechanism with vinyl
comonomers are given. Anionic copolymerization of elemental
sulfur with thiiranes e.g. propylene sulfide and isobutylene
sulfide has been described. Application of anionic initiators
in hydrocarbon solvents (e.g. benzene, toluene) leads to high-
-molecular weight copolymers ($\overline{M}_n$>10000) with sulfur content
in the copolymers reaching 85%.
Laser Raman Spectroscopy (LRS) and ^{1}H- and ^{13}C-NMR spectra
were used in determination of the structure of copolymers.
LRS allowed to show, that elemental sulfur is not present in
copolymers.
Kinetics of copolymerization was studied and the pertinent
kinetic scheme is described, giving access to the ratios of
the rate constants. Kinetic analysis has shown that the reac-
tivities of sulfur and propylene sulfide towards thiolate
anion are close to each other.

INTRODUCTION

Free-Radical Polymerization and Copolymerization of Elemental Sulfur

Commercial sulfur almost exclusively consists of an eight-atomic cyclic mo-
lecule (cycloocta-S, S_8), crystallizing orthorombically (S_α). This orthorom -
bic crown-shaped cyclooctasulfur is the only form thermodynamically stable at
room temperature (up to 95°). On heating above 95° orthorombic cyclloocta-S is
converted into monoclinic (S_β) cyclloocta-S, then, at 119.3° (melting point of
monoclinic S_8) it melts (Ref.1).
S_8 - an eight-membered ring - should be stable in different steric forms,
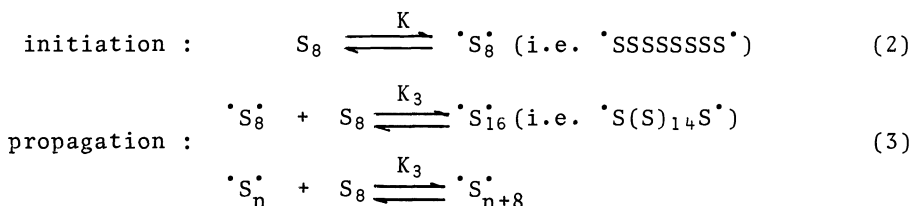but only the crown shape is known :
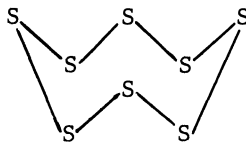
At the melting point the melt predominantly consists of free S_8 units. Further
heating results in darkening of the originally yellow melt and the mobile
liquid becomes viscous. These two phenomena start to become apparent above
159°, and are due to the conversion of S_8 into a high polymer :

$$\frac{n}{8} S_8 \rightleftharpoons \ldots{-}S_n{-}\ldots \qquad (1)$$
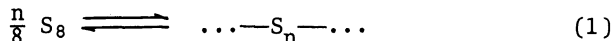
At the maximum viscosity, caused by increasing polymerization, the viscous
liquid contains macromolecules with units >100000 S_8 ($\overline{M}_n$>10^6) (Ref.2).
Further heating leads to depolymerization of the polymer and at the boiling
point (444°) finally a fairly fluid low - molecular weight (<S_{12}) liquid
exists (Ref.1).
Viscous liquid consists of a solution of polymeric linear polysulfur in S_8.

Polymerization apparently proceeds by homolytic scission of S_8 and its addition, in propagation, to polysulfur macroradicals. Fast quenched from the melt this solution converts into an elastic material, from which S_8 can be removed by extracting with CS_2. The rest is a polysulfur, having $T_g=75°$ (Ref. 1). This material can be stabilized against depropagation by reacting with some olefinic compounds, apparently, in this way some of the free radical chain ends are converted into the addition product less vulnerable and less able to start the unzipping process. The commercial product Crystex(R), used in vulcanization of unsaturated rubbers as a source of elemental sulfur has apparently a structure of linear polysulfur.

Tobolsky and Eisenberg successfully described the heat induced equilibrium polymerization of elemental sulfur, by making a distinction between the initiation process and propagation (Ref.3 & 4 & 5) :

$$\text{initiation :} \qquad S_8 \underset{\xleftarrow{\hspace{1cm}}}{\overset{K}{\xrightarrow{\hspace{1cm}}}} {}^{\bullet}S_8^{\bullet} \text{ (i.e. } {}^{\bullet}SSSSSSSS^{\bullet}) \qquad\qquad (2)$$

$$\text{propagation :} \qquad
\begin{aligned}
{}^{\bullet}S_8^{\bullet} + S_8 &\underset{\xleftarrow{\hspace{0.8cm}}}{\overset{K_3}{\xrightarrow{\hspace{0.8cm}}}} {}^{\bullet}S_{16}^{\bullet} \text{ (i.e. } {}^{\bullet}S(S)_{14}S^{\bullet}) \\[4pt]
{}^{\bullet}S_n^{\bullet} + S_8 &\underset{\xleftarrow{\hspace{0.8cm}}}{\overset{K_3}{\xrightarrow{\hspace{0.8cm}}}} {}^{\bullet}S_{n+8}^{\bullet}
\end{aligned}
\qquad\qquad (3)$$

Thus, the radical homopolymerization of elemental sulfur has been described as a living, reversible process, with equilibrium constants differing for the first step (K for homolytic scission of S_8 and formation of the first diradical) and all of the other steps (K_3), in which macroradicals add reversibly S_8.

The Tobolsky-Eisenberg theory (T-E theory) accounted well for a number of experimental findings, including dependence on temperature of polymer yield, its $\overline{DP}_n$ (Ref. 2 & 6), and concentration of free radicals, measured by ESR (Ref. 7).

For initiation $\Delta H_i^O = 105$ kJ.mol^{-1}, $\Delta S_i^O = 96$ J.mol^{-1}.K^{-1}, for the propagation process $\Delta H_p^O = 9.50$ kJ.mol^{-1}, $\Delta S_p^O = 22.9$ J.mol^{-1}.K^{-1}.

Unfortunately, polysulfur, as follows from its $T_f = 159°$ and as can be deduced from the above listed thermodynamic data, is unstable below its floor temperature, and converts by unzipping process into S_8 :
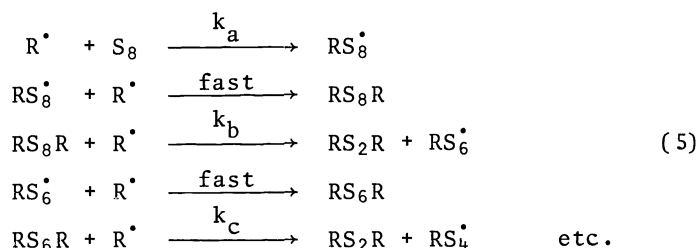
$$\ldots\text{-SSSSSSSSSSSSS}^{\bullet} \longrightarrow \ldots\text{-SSSSS}^{\bullet} + S_8, \text{ etc.} \qquad (4)$$
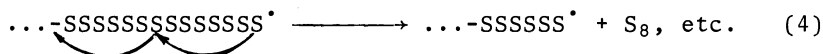
Breaking of the S-S bond in the polymer ($\Delta H_{s-s}^{\ddagger}$) requires approx. 130 kJ.mol^{-1} and $\Delta H_d^{\ddagger}$, the unzipping activation energy, equals 13 kJ.mol^{-1}. Thus, once the chain is broken, the monomer (S_8) is split off very easily.

Free-Radical Copolymerization of Elemental Sulfur

Stabilization of polysulfur chains against the unzipping process can be visualized by introducing into the chain foreign units that would stop the chain depropagation process. Copolymerization of S_8 should lead to polymers of this structure.
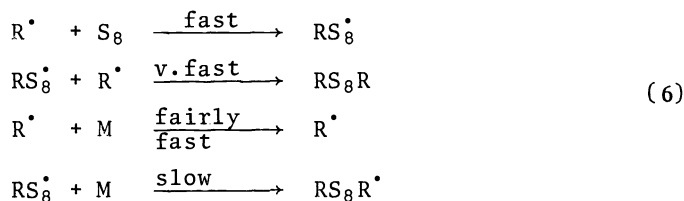
Preparation however of copolymers with olefinic comonomers was mostly unsuccessful (Refs. 8 - 10), tetrafluoroethylene being an exception and giving high polymers (Ref. 11). Attempted copolymerization of sulfur with styrene (Ref. 8) or vinyl acetate (Ref. 9) led either to the high polymers with low sulfur content, when small concentration of sulfur was used or, for higher starting concentration of sulfur, only low molecular weight oligomers were produced (e.g. $\overline{M}_n$ below 4000 for 10% wt.of sulfur in polystyrene). Induction periods were observed and decreased rates of polymerization. Thus, sulfur rather is considered to be an efficient inhibitor. This chain breaking mechanism was described by Bartlett (Ref. 8) by the following kinetic scheme:

$$R^{\cdot} + S_8 \xrightarrow{\quad k_a \quad} RS_8^{\cdot}$$

$$RS_8^{\cdot} + R^{\cdot} \xrightarrow{\quad fast \quad} RS_8R$$

$$RS_8R + R^{\cdot} \xrightarrow{\quad k_b \quad} RS_2R + RS_6^{\cdot} \qquad\qquad (5)$$

$$RS_6^{\cdot} + R^{\cdot} \xrightarrow{\quad fast \quad} RS_6R$$

$$RS_6R + R^{\cdot} \xrightarrow{\quad k_c \quad} RS_2R + RS_4^{\cdot} \qquad etc.$$

Each step in which sulfur or a polysulfide reacts with a free radical is thus regarded as a displacement of sulfur on sulfur by carbon, a reaction which becomes slower as the S-S bond acquires the heightened strength characteristic of the shorter polysulfides.

The ratios of k_a/k_p and k_b/k_p, where k_p is a rate constant of propagation, are close 10^2 for vinyl acetate and styrene, indicating high tendency of sulfur to inhibit polymerization. The rate constant of reaction of sulfur radicals with styrene or vinyl acetate are much lower than the rate constants of the corresponding homopropagations. Thus, sulfur is mostly added with a rate constant k_a but then the octasulfide bridges formed by recombination with $R^{\cdot}$ become reduced to the shorter ones by subsequent reactions with macroradicals $R^{\cdot}$.

Thus, the attempted copolymerization of sulfur with vinyl monomers is prohibited, because of the low reactivity of sulfur radical towards vinyl monomers. This can be illustrated by scheme (6) below :

$$R^{\cdot} + S_8 \xrightarrow{\quad fast \quad} RS_8^{\cdot}$$

$$RS_8^{\cdot} + R^{\cdot} \xrightarrow{\quad v.fast \quad} RS_8R$$

$$R^{\cdot} + M \xrightarrow{\quad fairly \atop fast \quad} R^{\cdot} \qquad\qquad (6)$$

$$RS_8^{\cdot} + M \xrightarrow{\quad slow \quad} RS_8R^{\cdot}$$

It has to be stressed, however, that although the polysulfide radical $RS_x^{\cdot}$ (e.g. $RS_8^{\cdot}$) can not enter into chain propagation the thiyl radical $RS^{\cdot}$ reacts easily with vinyl monomers.

ANIONIC COPOLYMERIZATION OF ELEMENTAL SULFUR

General considerations

The inability of sulfur (described in the previous section) to   copolymerize with simple vinyl monomers stems from the insufficient reactivity of the polysulfide radical $RS_x^{\cdot}$ towards these monomers. Thus, it occured to us, that in order to force sulfur to copolymerize it would be necessary to have both active species of as similar as possible structures. Although there are some other possibilities that are currently being tested in this laboratory, but this general approach, the first one that allowed sulfur to copolymerize successfully with organic monomers (copolymerization with inorganic ones, like selenium and phosphorus, has been known for a long time (Refs. 12 & 13)) will be discussed in this paper exclusively.

Attempted copolymerization of sulfur with cyclic sulfides, namely propylene sulfide and isobutylene sulfide, described first in our patent we applied for in 1972 (Ref.14), was an immediate success. Copolymers with long sulfur sequences (up to 85% wt. of sulfur content) were obtained.

Copolymers of sulfur with propylene sulfide (Refs. 15 & 16)

Copolymerization was carried out in benzene or toluene solution and was initiated either with $CdCO_3$ (insoluble in the polymerizing mixture) or with soluble thiolates (e.g. crowned sodium thiophenolate).

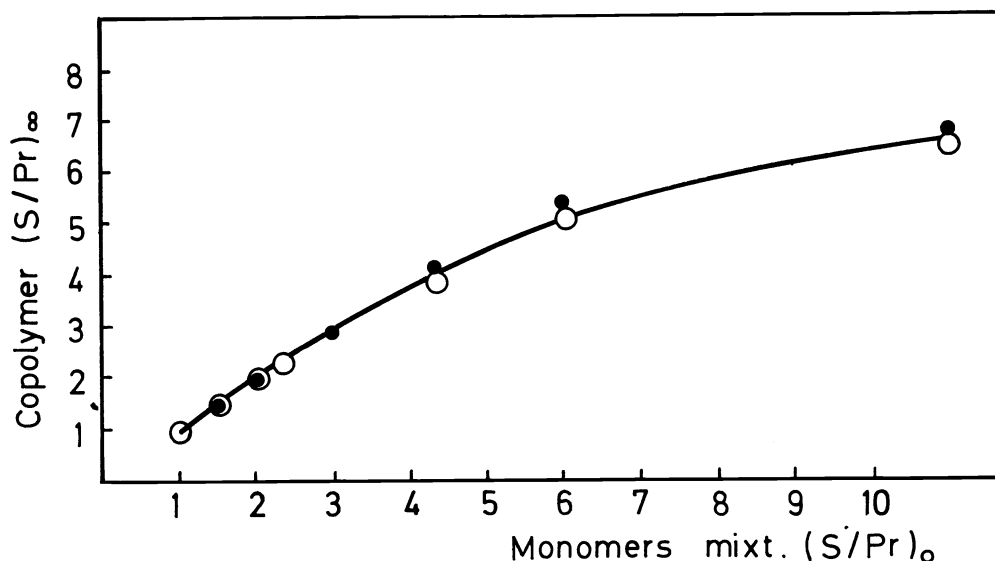Dependence of copolymer composition on monomer composition is shown in Fig.1.

Fig. 1. Dependence of composition of propylene sulfide with
elemental sulfur on the ratio of comonomers.
○ : elemental analysis; ● : Laser Raman Spectra.

The dependence in Fig.1 was obtained for copolymerization of propylene sulfi-
de (P) and sulfur taken in concentrations : $[PS]_o$=0.2 mol/l ÷ 2 mol/l

and $[S_8]_o$=2 mol/l respectively, at 80°C in benzene solution. Copolymers were
extensively extracted with hot methyl alcohol, dissolving sulfur (solubility
0.082g/100g at 62°) (Ref. 17) but not dissolving copolymers. The absence of ele-
mental sulfur in copolymers was proved by Laser Raman spectra. It is known,
that elemental sulfur gives in Raman two strong bands at 217 and 475 cm^{-1}
(Ref. 18); these bands disappear during copolymerization and are no more
present in purified copolymers. This observation makes it clear, that sulfur
in copolymers does exist as sulfur chemically bound, i.e. in polysulfide
bridges, and that sulfur that could have been present as a solid solution is
absent.
Composition of copolymers was determined in two ways: by elemental analysis
of purified samples and by following by LRS the copolymerization process and
assuming that the reacted (according to LRS) S_8 has been introduced into co-
polymer. Agreement between these two methods, as judged from Fig.1,is quite
satisfactory.
Actually, our attempts to obtain copolymers of sulfur and propylene sulfide
by reacting independently prepared poly(propylene sulfide) with S_8 at the
usual copolymerization conditions were unsuccessful. The only polymeric pro-
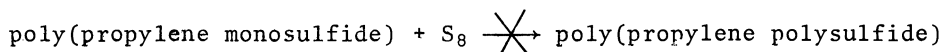duct isolated was the starting poly(propylene sulfide),

poly(propylene monosulfide) + S_8 →✕→ poly(propylene polysulfide)

Fig.1 shows that the content of sulfur in copolymers does depend on the mono-
mer feed, i.e. the ratio of S_8 to propylene sulfide. However, it seems that
there is a limit of the length of the polysulfide bridges, close to 8÷9
atoms of sulfur :

$$\begin{array}{c} CH_3 \\ | \\ (CH_2\text{-}CH\text{-}S_{8-9})_n \end{array}$$
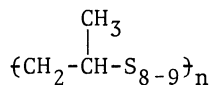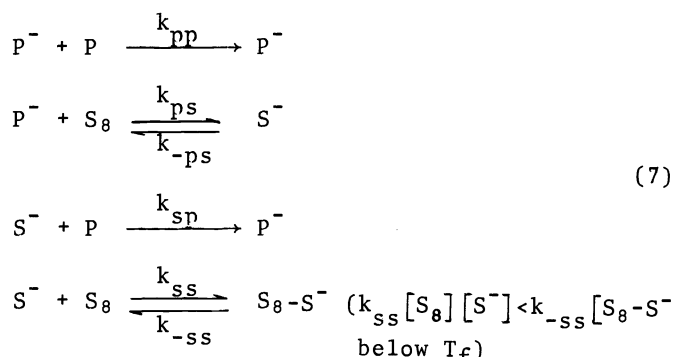
It will become apparent from the text below   , that this is a result of con-
ducting copolymerization below the floor temperature T_f of homopolymerization
of S_8; i.e. at the conditions, when S_8 cannot homopolymerize, because the
rate of propagation becomes at T_f equal to the rate of depropagation.
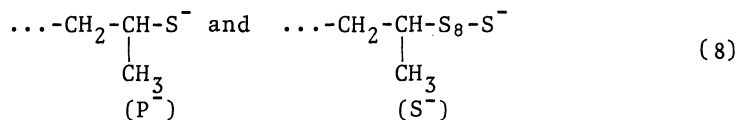
Kinetics of Copolymerization (Ref. 16)

Kinetics of copolymerization of S_8 with P has been studied by combined LRS
and ^{1}H-NMR methods. Copolymerization was initiated with sodium thiophenolate;
sodium cation was crowned with dibenzo-18-crown-6 ether. Analysis of kinetic
curves led to the following conclusions :
a. Linearity of semilogarithmic anamorphoses suggests the "living" character
   of copolymerization. This could have been expected since the anionic poly-
   merization of P is also living at the properly chosen conditions (Ref.19).

b. Slopes of these linear anamorphoses decrease with increasing proportion of
   S_8 in the monomer feed. This means, that the longer the polysulfide chain
   preceding the active species the lower the reactivity of this species.
   Apparently, the electron pair of the thiolate anion interacts with sulfur
   atoms preceding the anion. This interaction increases with a length of the
   polysulfide chain.

Kinetic scheme can tentatively be described by the following set of equations:

$$P^- + P \xrightarrow{\ k_{pp}\ } P^-$$

$$P^- + S_8 \xrightleftharpoons[k_{-ps}]{k_{ps}} S^-$$

(7)

$$S^- + P \xrightarrow{\ k_{sp}\ } P^-$$

$$S^- + S_8 \xrightleftharpoons[k_{-ss}]{k_{ss}} S_8\text{-}S^- \quad (k_{ss}[S_8][S^-] < k_{-ss}[S_8\text{-}S^-]$$
$$\text{below } T_f)$$

Scheme (7) does not take into account the dependence of reactivity of S^- on
the number of sulfur atoms preceding this species. In other words, it assumes,
that there are only two kinds of growing species, namely

$$\ldots\text{-CH}_2\text{-CH-S}^- \quad\text{and}\quad \ldots\text{-CH}_2\text{-CH-S}_8\text{-S}^-$$
$$\qquad\quad |\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\quad \text{CH}_3\qquad\qquad\qquad\qquad \text{CH}_3$$
$$\qquad\quad (P^-)\qquad\qquad\qquad\qquad\ (S^-)$$

(8)

Scheme (7) corresponds to the related set of differential equations :

$$-\frac{d[P]}{dt} = k_{pp}[P^-][P] + k_{sp}[S^-][P]$$

(I)

$$-\frac{d[S]}{dt} = k_{ps}[P^-][S_8] - k_{-ps}[S^-]$$

and

$$-\frac{d[P^-]}{dt} = k_{ps}[P^-][S] - k_{-ps}[S^-] - k_{sp}[S^-][P]$$

(II)

$$-\frac{d[S^-]}{dt} = k_{sp}[S^-][P] + k_{-ps}[S^-] - k_{ps}[P^-][S]$$

Assuming steady state conditions for both kinds of active species, and put-
ting :

$$r = k_{pp}/k_{ps} \qquad\text{and}\qquad \rho = k_{-ps}/k_{sp}$$
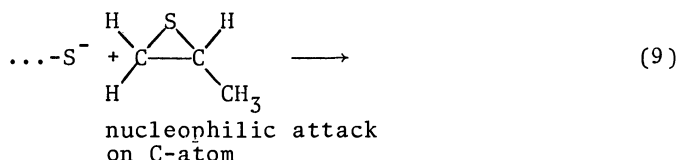
(III)

we have :

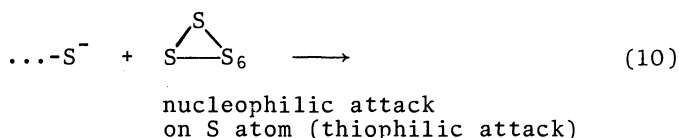$$\frac{[S]}{[P]} \left(\frac{d[S]}{d[P]} - 1 \right) = r + r\rho \, \frac{1}{[P]} \qquad\qquad (IV)$$

Experimental data were plotted according to Eq. (IV) (Ref.16) and the resulting straight-line dependence allowed to determine both r and ρ at 80° in benzene solution :

$$r = 1.3 \times 10^{-1} \qquad \text{and} \qquad \rho = 8.6 \times 10^{-3} \qquad (V)$$

Taking into account the statistical factor we find that propylene sulfide and elemental sulfur have similar reactivities towards thiolate anion. Discussion of any structure - reactivity relationship becomes however difficult, because these two monomers react with thiolate anion according to different mecha - nism:

$$...-S^- \; + \; \overset{H}{\underset{H}{\diagdown}}C \underset{}{\overset{S}{\triangle}} C \overset{H}{\underset{CH_3}{\diagup}} \longrightarrow \qquad (9)$$

nucleophilic attack
on C-atom

and :

$$...-S^- \; + \; S \overset{S}{\triangle} S_6 \; \longrightarrow \qquad (10)$$

nucleophilic attack
on S atom (thiophilic attack)

The thiophilic attack on S atom in S_8 can be a fast reaction, because sulfur is known to be able to expand its octet into decet. The p and d orbitals can participate in this process, lowering the energy of activation. This can counterbalance the release of strain of the three-membered ring of propylene sulfide, which can lower the energy of activation in comparison with the nucleophilic substitution of the non-strained compounds.

Microstructure of Copolymers and Scrambling Processes (Refs. 15 & 16)
Microstructure of copolymers of S_8 with P has been studied by ^{1}H- and ^{13}C-NMR methods . Poly(propylene monosulfide) gives in ^{1}H-NMR a characteristic doublet for $\underline{CH_3}$ protons (1.3 and 1.4 δ). In copolymers (i.e. poly(propylene polysulfides)) the $\underline{CH_3}$ protons give a multiplet. At lower proportion of S in copolymers this multiplet resembles superposition of four lines (e.g. two doublets), two of these lines have chemical shifts at 1.3 and 1.4 δ, chara - cteristic for a homopolymer, and the two other lines are shifted upfield, as it could be expected (Refs. 20 & 21) for $\underline{CH_3}$ protons in β-position to the po- lysulfide linkage.
^{13}C-NMR spectrum also indicates the presence of the polysulfide bridges. $\underline{CH_3}$ carbon atoms in poly(propylene monosulfide) absorb at 20.7 δ whereas in po- ly(propylene pentasulfide)

$$\underset{}{\overset{CH_3}{\underset{|}{\{CH_2-CH-S_5\}_n}}}$$
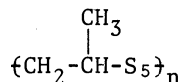
(where 5 is an average number)
prepared by polycondensation of 1,2-dichloropropane and sodium pentasulfide, absorption at 20.7 δ disappears and a new singlet appears at 19.4 δ.
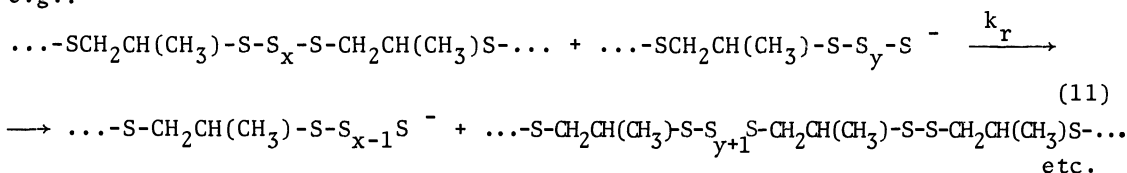In copolymers with an average length of polysulfide bridges $\bar{x}=2$:

$$\underset{}{\overset{CH_3}{\underset{|}{\{CH_2-CH\{S\}_{\overline{x}}\}_n}}} \; , \; \text{where} \; \bar{x}=2$$
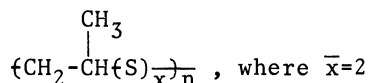
both singlets, at 19.4 δ and 20.7 δ, have almost the same intensity. This means, that S_8 added to ...-S^- and forming eventually the ...-S_9-... unit becomes further reorganized and cut into shorter segments. Otherwise singlets at 19.4 δ and 20.7 δ should rather be (even taking into account the NOE effect) close to 1:10 and not, as mentioned above, 1:1.

The mechanism of this redistribution of the polysulfide bridges can be pre -
sented as the nucleophilic (thiophilic) attack of thiolate anion on the po -
lysulfide sequences in the already formed copolymer :

e.g.:

$$...-SCH_2CH(CH_3)-S-S_x-S-CH_2CH(CH_3)S-... + ...-SCH_2CH(CH_3)-S-S_y-S^- \xrightarrow{k_r}$$

(11)

$$\longrightarrow ...-S-CH_2CH(CH_3)-S-S_{x-1}S^- + ...-S-CH_2CH(CH_3)-S-S_{y+1}S-CH_2CH(CH_3)-S-S-CH_2CH(CH_3)S-...$$

etc.

Rate constant of reshuffling k_r can even be higher than the rate constant of
reaction of a similar thiolate anion with S_8.
This fast process of reshuffling leads eventually to the averaging of the po-
lysulfide bridges and to establishing the thermodynamic distribution from the
kinetically given mono- and nonasulfide linkages. We have at present no in -
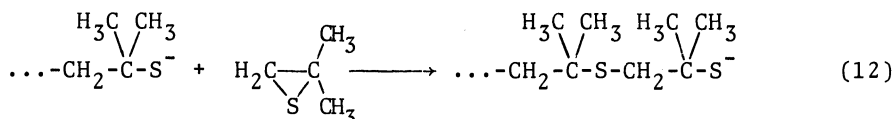formation on the thermodynamic distribution.
The proposed in this section redistribution, accounting for the observed
^{13}C-NMR spectra, is in contradiction with the proposed kinetic scheme with only
two kinds of growing centers : $-...S_1^-$ and $-...S_9^-$. Of course, during copolyme-
rization these species will be converted into species $-...S_x^-$ with a certain
distribution of the number of sulfur atoms (x-1) preceding the thiolate anion.
However, at the early stages of copolymerization there is a large excess of
$|S_8|$ over the concentration of polysulfide bridges in macromolecules. Thus,
one can assume, that the rate of addition of S_8 is faster than the rate of
reshuffling and, at least for the early stages of copolymerization the propo-
sed kinetic scheme is valid.

Copolymerization of Izobutylene Sulfide (B) with S_8
Copolymerization of izobutylene sulfide with S_8 proceeds
as copolymerization of S_8 with propylene sulfide. The products of the reac -
tion are rubber-like solid materials, soluble in benzene at room temperature,
whereas homopolymer of B (poly B), obtained using anionic initiators, is a
crystalline product insoluble in benzene. A comparison of the ^{1}H-NMR spectra
of poly B with copolymer clearly indicates the formation of true copolymers
with a statistical distribution of the polysulfide units.
The spectrum of poly B contains two peaks 1.4 δ (protons of CH_3) and 2.85 δ
(protons of CH_2). This shows that poly B practically does not contain head-to-
-head and tail-to-tail linkages in the main chain, as it was generally obser-
ved in the anionic polymerization of thiiranes (Ref. 23 & 24). This indicates
that under these conditions a nucleophilic attack proceeds exclusively at the
methylene carbon atom :

$$...-CH_2-\overset{\overset{\displaystyle H_3C \diagup CH_3}{\diagup}}{C}-S^- + H_2C\overset{\overset{\displaystyle CH_3}{\diagup}}{\underset{\underset{\displaystyle S \quad CH_3}{\diagdown\diagup}}{C}} \longrightarrow ...-CH_2-\overset{\overset{\displaystyle H_3C \diagup CH_3}{\diagup}}{C}-S-CH_2-\overset{\overset{\displaystyle H_3C \diagup CH_3}{\diagup}}{C}-S^-$$

(12)

This is in agreement with other nucleophilic displacement reactions of thi -
iranes (Ref. 25).
The protons of the methylene groups of copolymer with $\bar{x}=2.6$ appear as a multip-
let in the region of 3.36 δ to 3.6 δ which seems to be due to an overlap of
at least three singlets. It is remarkable that there is practically no mono -
sulfide function in the copolymer (absence of the singlet at 2.85 δ).
The chemical shifts of protons in methylene groups joined by a polysulfide
sequence, are known to depend on the number of sulfur atoms in the polysul-
fide bridge (Ref. 20 & 21). The larger the polysulfide sequence the more
downfield shifted are the signals of the methylene protons.
A comparison of the concentration of sulfur incorporated into the copolymer
(from LRS) with the intensity of these separated singlets in the region of
methylene protons allowed us to assign tentatively the corresponding singlets
to methylene groups linked to a given number of sulfur atoms in the adjacent
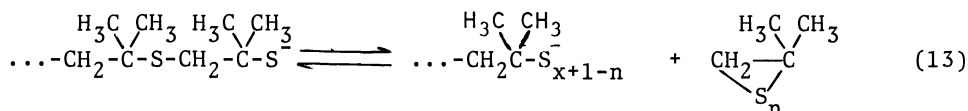polysulfide bridge (Tab. 1).

TABLE 1. Dependence of the chemical shift of methylene protons on the number of adjacent S-atoms in the repeating units of copolymer

| | $(\ldots-CH_2-S_x-\ldots)$ | | | |
	x=1	2	3	4
δ in ppm	$2.85^{a)}$	3.36	3.47	3.60

In the ^{1}H-NMR spectrum of the polymerizing mixture there are additionally two peaks arising from methylene : 3.27 δ and methyl protons : 0.99 δ, which can neither be deduced from the homopolymer nor from the copolymer. On the other hand, in the Raman spectra signals are observed at 238 and 464 cm^{-1} in the region of the Raman scattering of cyclic low-molecular polysulfides. Fehér has observed (Ref. 26) that the spectrum of the cyclic pentasulfide, 3,4,5, 6,7-pentathiatricyclo[7.2.1.0^{2,8}]dodec-10-ene:
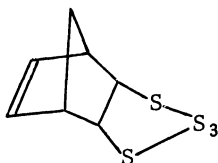
shows two strong bands at 236 and 462 cm^{-1}, very close to the bands observed in the spectrum of the copolymerizing mixture. The singlets 0.99 δ and 3.27 δ in the ^{1}H-NMR spectrum change their intensity during the copolymerization in a similar way as the Raman bands do. Thus, we tentatively assume, that a cyclic polysulfide is formed from S$_8$ and B at the early stage of copolymerization and then disappears, if a sufficient excess of B is used.
Cyclic polysulfides, observed by Raman and ^{1}H-NMR spectrum, might be formed in an intramolecular reaction (eq.13) in which a thiolate anion attacks a penultimate sequence of the same copolymer chain (back-biting). This reaction may also be considered as an intramolecular scrambling :

$$\ldots-CH_2-\underset{\underset{CH_2}{|}}{\overset{\overset{H_3C \diagdown \diagup CH_3}{|}}{C}}-S-CH_2-\underset{\underset{}{|}}{\overset{\overset{H_3C \diagdown \diagup CH_3}{|}}{C}}-S^- \rightleftharpoons \ldots-CH_2-\overset{\overset{H_3C \diagdown \diagup CH_3}{|}}{C}-S^-_{x+1-n} \quad + \quad \underset{S_n}{\overset{H_3C \diagdown \diagup CH_3}{CH_2-C}} \qquad (13)$$

Data presented in this paper show that elemental sulfur can indeed be copolymerized with cyclic sulfides by anionic mechanism. High molecular weight polymers prepared by the methods described in this paper are elastomeric and their sulfur content can be as high as 85% wt. However, the proper conditions have to be used (initiator, solvent, temperature), because otherwise from the same monomer feed merely polysulfides with limited $\overline{x}$ are formed. Temperature is particularly important, because one of the comonomers (S$_8$) is copolymerized below its T$_f$. Thus, for similar conditions, the copolymer composition (i.e. equilibrium concentration of S$_8$) would depend on temperature. The higher the temperature the lower the equilibrium concentration of S$_8$. The too low temperature is probably a reason, that copolymers with high sulfur content could not be obtained, when copolymerization of P and S$_8$ was attempted by Krentzel et al. (Refs. 27 - 29). Another important factor is the starting concentration of sulfur ([S$_8$]$_0$).

One can expect that a number of new monomers, cyclic sulfides as well as monomers belonging to other classes of chemical compounds will be found to copolymerize with elemental sulfur. This became possible since it has been understood that the major factors allowing this copolymerization to proceed are : similar reactivities of both growing species and the thermodynamic requirements, due to the reversibility of S$_8$ homopropagation.

Note   a.   Absent in copolymer

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