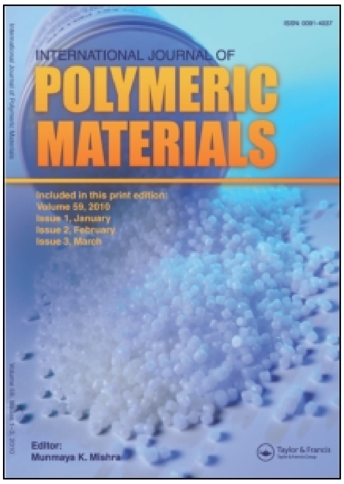

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Thermal and Thermochemical Conversion of Aliphatic Polysulfide Elastomers

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Thermal and Thermochemical Conversion of Aliphatic Polysulfide Elastomers

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The destruction of a number of linear and structuring polysulfide elastomers prepared on the (bis-(2-chlorethyl)formal basis in vacuum and in an oxygen medium in the temperature range 140 to 260°C is discussed.

The peculiarities of the destruction processes of aliphatic polysulfides in vacuum and under thermal oxidation conditions are considered.

The dependence of thermal resistance on the structure of the elementary polymer link is established.

The scheme for thermal and thermal-oxidative destruction of polysulfides, supported by NMR, EPR, IR-spectroscopy and mass spectrometry data is suggested.

KEYWORDS: Polysulfide, elastomers, thermodegradation, chemical conversion, structure, properties, mechanism

Aliphatic polysulfide rubbers are highly-resistant to many chemically agressive media and have a low rate of ageing under the action of different factors. These polyfulfide properties allows utilizing them as rubber material for special purpose.

Therefore, the study of thermal properties of polysulfide rubbers and the dependence of thermal resistance on their structure is of exceptional interest.

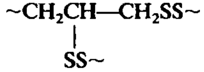
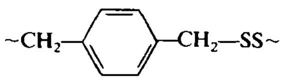
The investigated polymers and copolymers were synthesized by the method of suspension polycondensation of the corresponding dichloriderivatives with sodium polysulfide.[1]

The structure of the sample polymers is given in Table I.

The thermal destruction of the polysulfide was studied in vacuum of 10^{-3} mm Hg, in the temperature range 125 to 260°C, during 1 heating hour at each temperature in a closed system, vol. 0.08 l, supplied with a mercury gauge and special tap to take the gas sample during the experiment for chromatographic analysis of the gaseous destruction products.

TABLE I

Structure of sample polymers

Polymer number	Structure formula of polymer[a] and copolymer	
I	$\sim CH_2CH_2OCH_2OCH_2CH_2SS\sim$	
II	$\sim CH_2CH_2OCH_2OCH_2CH_2SS\sim$ $\sim CH_2\underset{\displaystyle SS\sim}{CH}—CH_2SS\sim$	96% 4%
III	$\sim CH_2CH_2OCH_2OCH_2CH_2SS\sim$ $\sim CH_2CH_2SS\sim$	50% 50%
IV	$\sim CH_2CH_2OCH_2OCH_2CH_2SS\sim$ 	80% 20%

[a] —OH end groups.

The thermal oxidative destruction was carried out in sealed ampoules containing dry oxygen under 150 mm Hg, comprising 2 moles per elementary polymer link.

The gaseous destruction products were analyzed on a LKhM-8MD chromatograph. The analysis of CO_2, COS, H_2O, SO_2 and C_2H_4 was made on a 1 m column, 0.3 cm diameter packed with Parapack—*Q*, column temperature—70°C, carrier gas—helium; CO and CO_2 were chromatographed on a column packed with activated carbon at room temperature.

The IR-spectra of the gas phase were recorded in a special convette on a IR-10 spectrometer in the 400–3700 cm^{-1} band.

The mass-spectra of the liquid and solid destruction products were recorded on an AEI-MS-30 mass-spectrometer using the direct introduction of the sample into the ion source and stepwise raising of the temperature of the pyrolitic cell up to 250°C. The ionizing radiation was 70 and 20 volt, the ionizing chamber temperature 250°C.

The EPR-spectra of the destruction products were taken with a JES-ME-3x apparatus.

The ^{1}HNMR spectra of the liquid and solid destruction products of polysulfide rubbers were recorded in carbon bisulfide, using a "Bruker WR-200-SI" spectrometer (200, 13 mHz), tetramethilsilane being the inner standard.

^{1}HNMR spectrum I (δ, m.g.): 5.03C (2H, $C^{①}H_2$), 4.19*t* (2H, $C^{②}H_2$) $I = 6.0$ Hz, 3.19*t* (2H, $C^{③}H_2$, $I = 6.0$ Hz).

^{1}HNMR spectrum II (δ, m.g.): 4.88C (2H, $C^{①}H_2$), 4.20*t* br (4H $C^{②}H_2$ and $C^{⑤}H_2$, $I = 5.2$ Hz), 3.12*t* (4H, $C^{③}H_2$ and $C^{④}H_2$, $I = 5.2$ Hz).

The investigation of polysulfides destruction in vacuum has shown that they are stable up to 140°C, but at 100°C the weight loss amounts to 16.0; 11.9; 14.3; 6.8 wt% for polymers I, II, III and IV respectively; at 250°C the polymers decompose 80–90% (Figure 1, Table II).

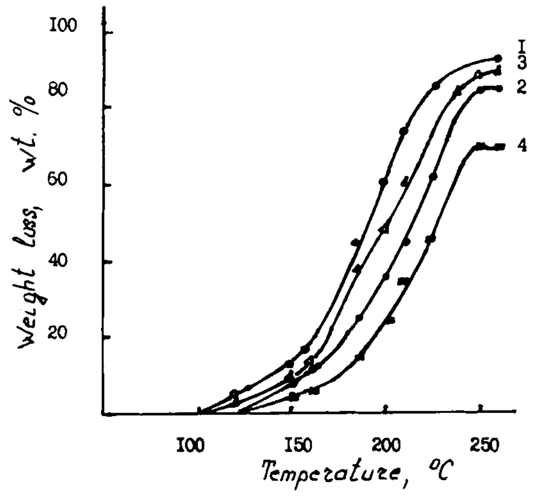


FIGURE 1 Conversion depth during thermal destruction of polysulfides: 1—I, 2—II, 3—III, 4—IV.

The most thermal-resistance appeared to be polymer IV, containing aromatic fragments in its structure, the least thermal-resistant was polysulfide I.

Liquid and solid low-molecular compounds comprised the main faction of the destruction products of the sample polymers. The composition of these compounds was partially identified by the method of mass-spectroscopy.

Since the fragments replicating the elementary polymer I link are similar and predominant in structure of all the polysulfides, this polymer in particular was most comprehensively studied. The mass-spectra of the liquid and solid products destruction as well as other compounds which were under experimental conditions in a vapour state, and condensed in a trap and cooled with liquid nitrogen have been recorded.

The mass-spectra of the liquid and solid products revealed oligomeric compounds comprising 2–3 elementary links, as well as compounds with masses 166, 122, 92 which can be attributed to the structures indicated in Table III.

Substances with mass numbers 45, 46, 60, 92 (Table III) are predominant in the mass-spectra of the condensed fraction. Besides, the mass-spectra of both fractions reveal masses of 32 and 64 which correspond to ionic and molecular sulfur as well as mass peaks of 30, 31 and 18 which can be attributed to formaldehyde and water.

The presence of acetaldehyde and formaldehyde in the polymer I thermolysis products were supported by the IR-spectra of the gaseous fraction.

The absorbance bands at 1740 cm^{-1} in the spectra correspond to the stretching mode of the CO-group, the doublets at 2900 and 2720 cm^{-1} to the deformation mode of the CH-bond.[2,3]

Some of the mass peaks can be attributed both to the mercaptan and to the cyclic mono- and disulfide structures, respectively. However, according to the

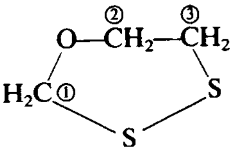
TABLE II

Composition of low-molecular products of thermal destruction of polysulfides during 1 hour heating at each temperature

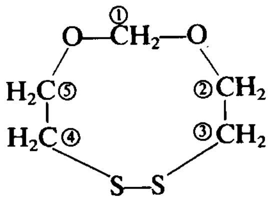
Polymer number	Destruction temperature °C	Total weight wt%	Amount of liquid and solid wt%	Amount of gaseous wt%	Gaseous destruction products mole/basically mole			
					C_2H_4	H_2S	COS	Sum of carbon oxide
I	150	11.25	11.25	—	—	—	—	—
	160	16.10	16.10	—	—	—	—	—
	185	43.90	43.90	—	traces	—	—	—
	210	74.70	74.72	0.08	0.01	—	—	—
	225	86.50	83.41	3.09	0.01	0.06	—	0.05
	235	90.30	95.69	4.61	0.02	0.13	traces	0.05
	250	93.20	86.78	6.42	0.02	0.21	0.01	0.05
	260	93.80	83.24	10.56	0.02	0.43	0.01	0.05
II	150	9.90	7.50	—	—	—	—	—
	160	10.55	10.55	—	—	—	—	—
	185	22.60	22.60	—	—	traces	—	—
	210	45.50	44.52	0.98	traces	0.05	traces	—
	225	63.00	59.81	3.19	0.02	0.12	0.01	0.01
	235	75.10	68.92	6.18	0.02	0.20	0.02	0.04
	250	85.60	84.90	10.70	0.03	0.34	0.02	0.09
	260	86.30	74.50	11.80	0.03	0.39	0.02	0.09
III	150	7.50	9.90	—	—	—	—	—
	160	14.30	14.30	—	—	—	—	—
	185	38.14	38.14	—	—	traces	—	—
	210	59.50	57.31	2.19	0.01	0.08	—	—
	225	73.40	69.21	4.19	0.03	0.13	—	traces
	235	83.00	75.13	7.87	0.04	0.25	traces	traces
	250	89.45	77.46	11.99	0.07	0.37	0.02	0.01
	260	90.10	73.43	16.67	0.09	0.53	0.02	0.02
IV	150	4.20	4.20	—	—	—	—	—
	160	6.90	6.90	—	—	—	—	—
	185	14.55	14.55	—	—	traces	—	—
	210	35.30	33.36	1.94	traces	0.10	—	—
	225	46.00	39.31	6.69	traces	0.35	—	traces
	235	62.50	51.46	11.04	0.01	0.55	—	traces
	250	70.56	52.30	18.26	0.01	0.85	0.01	0.04
	260	70.80	48.86	21.94	0.01	1.04	0.01	0.03

data presented in Refs 4 and 5 as well as to the possibility of polymerization of cyclic desulfides affected by impurities and exposed to light, one may expect the formation of cyclic products most probable.[6,7] The same conclusion can be made from the NMR data.

^{1}H NMR-spectra of solid and liquid destructure products of polysulfide elastomers at 250°C has shown that the destruction products mixture of about equal amounts contain compounds I and II having the following structures:



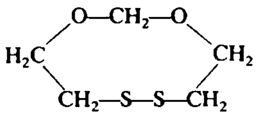
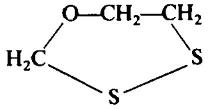
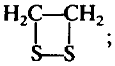
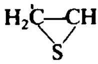
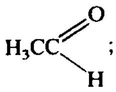
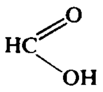
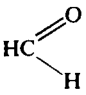
I



II

TABLE III

Possible compound structures corresponding to mass numbers of destruction products of polysulfide rubbers

Mass number	Possible structure of polysulfide destruction products
166	
122	 $H_3COCH_2OCH_2CH_2SH$ $H_3CCH_2SSCH_2CH_3$
92	 ; $H_3COCH_2CH_2SH$
60	 ; H_3CCH_2SH
44 45 46	 ;  ; CH_3CH_2OH
30	
18	H_2O

The IR-spectra of the destruction products failed to reveal any absorbance band at 2600–2500 cm^{-1} which would correspond to the stretching mode of the SH-bond.[8] However, the possibility of formation of products containing a mercapto-group should not be excluded.

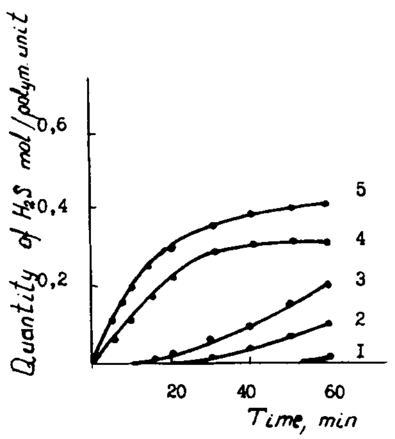


FIGURE 2 Kinetic curves for hydrogen sulfide evolution, in moles/basically moles, during polysulfide I destruction: 1—210°C, 2—225°C, 3—235°C, 4—250°C, 5—260°C.

Hydrogen sulfide present in large quantities in the gaseous destruction products (Table II). Besides H_2S, ethylene as well as small quantities of oxygen-containing gases CO_2, CO and COS were also detected.

In all probability, the formation of CO, CO_2 and COS is related to the destruction of the oxygen-containing groups which were formed in small amounts in aliphatic polymers storage.[9]

The same assumptions were made by the authors in Ref. 3 in which they

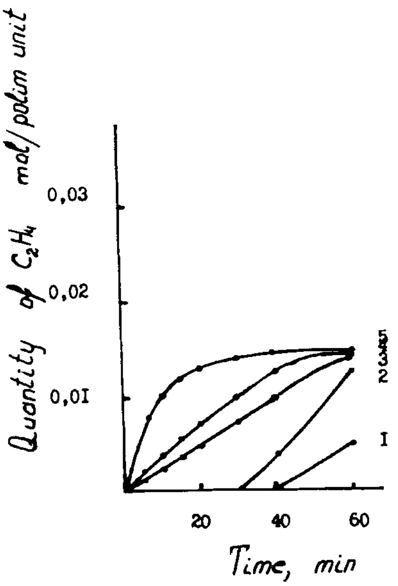


FIGURE 3 Kinetic curves for ethylene evolution, in moles/basically moles, during polysulfide I destruction: 1—210°C, 2—225°C, 3—235°C, 4—250°C, 5—260°C.

recorded the formation of CO, CO_2 and COS after polyethylensulfide thermal destruction.

It has been experimentally found that the great amount of carbon oxides is formed in the process of polymer II thermolysis, which contained in its structure tertiary carbon atoms which, as is known, undergoes, first of all, oxidation.[10,11]

Investigation of the kinetic of H_2S and C_4H_4 evolution during polysulfide destruction (I–IV) has shown that their formation proceeds with an induction period within the temperature range of 210–235°C. The kinetic H_2S and C_2H_4 gas-evolution curves are illustrated in Figures 2 and 3.

The kinetic data analysis supposes that the primary act of destruction of those polymers is, in all probability, a homolytic rupture on the basis of the —S—S— bond law forming polymer radicals of different lengths whose further destruction leads to to the formation of liquid, solid and gaseous products.

A great deal of hydrogen sulfide is formed in the thermolysis of polymer IV (Figure 4), though the activation energies of H_2S formation for all the polymers are practically the same, comprising 29, 28, 23 and 23 (±3) KCal/mol for polymers I, II, III and IV, respectively. This circumstance is probably related to the higher thermal resistance of polymer IV. As for polymers I, II and III, the fragmentation of the main link proceeds more readily, whereby the sulfur-containing fragments in its structure can be readily removed from the heating area, whereas in polysulfide IV the secondary reactions occur deeper, resulting in the formation of H_2S. It should be noted, that a great deal of the ethylene is detected in the polymer destruction products since they contain ethylensulfide links in their structure 30% (Figure 5).

The mass-spectrometric analysis of the polysulfides I, III and IV destruction products has shown that the set of destruction products for all investigated

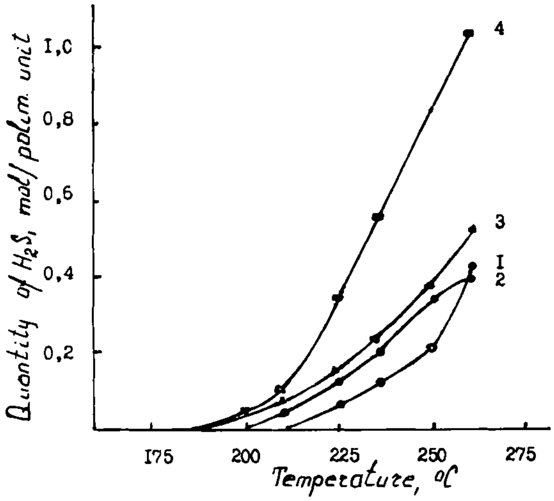


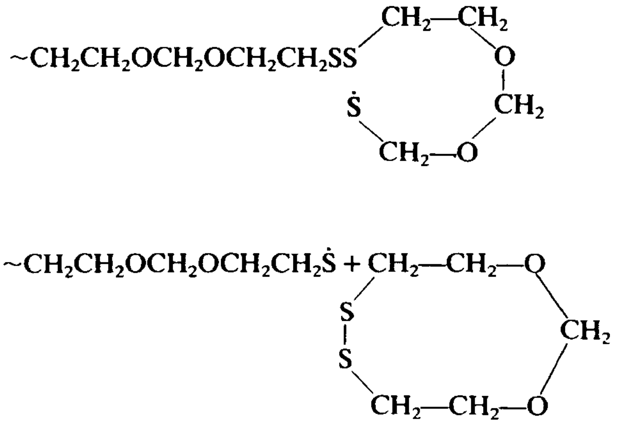
FIGURE 4 Hydrogen sulfide quantity formed during polysulfides destruction: 1—I, 2—II, 3—III, 4—IV vs. temperature.

polymers are the same. However, polymer I possesses to a great extent compounds with masses 122 and 166, while polysulfides III and IV contain largely compounds with masses 92, 60 and 45. This circumstance is likely due to the decrease in the number of fragments in the structure of polymers III and IV, $\text{—CH}_2\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{—S—S—}$, which lead to the formation of the basic compounds with masses 166 and 122. The circumstances that the peak intensities corresponding to the mass number 45 and 60 are lesser in the polymer IV destruction products that in those of polymer III is probably due to the higher thermal resistance of polymer IV which at 200°C decomposes to a lesser extent in the case of polymer III.

It should be noted that the intensity of mass 166 decreases with rising destruction temperature.

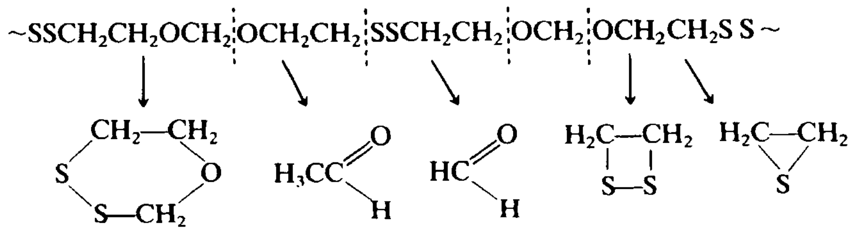
The analysis of the experimental data allows one to suppose the following thermal destruction scheme for aliphatic polysulfide rubbers.

In the relatively low temperature (up to 200°C), the rupture of the S—S bond and the elimination of the monomeric cyclic fragment occur according to the following scheme:



Probably, thionyl radicals which are formed during the dissociation of the S—H bonds of the residual thio end groups are responsible for the onset of depolymerization.

Alongside with depolymerization up to monomeric cyclic fragments, there takes place a rupture of the S—C and C—O bonds at higher temperature to form cyclic products of different structures:



Simultaneously with this, we assume that the gaseous products of polysulfide

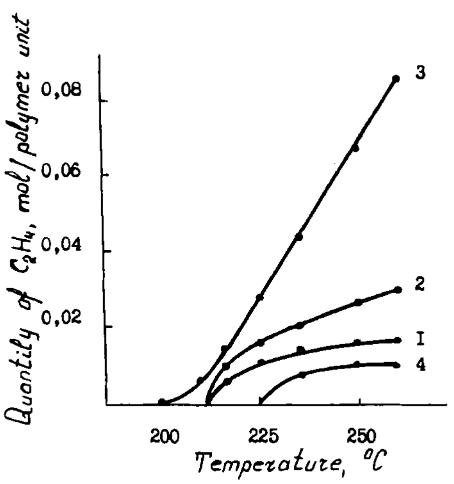


FIGURE 5 Ethylene quantity formed during polysulfides destruction in vacuum: 1—I, 2—II, 3—III, 4—IV vs. temperature.

destruction, such as hydrogensulfide and ethylene, can be formed at the expense of weak bonds rupture, according to the following scheme:

$$\sim SCH_2CH_2OCH_2OCH_2CH_2S\sim$$
$$\downarrow$$
$$\sim SCH_2\dot{C}H_2 + \dot{O}CH_2OCH_2CH_2S\sim$$
$$\searrow$$
$$\sim\dot{S} + \underline{CH_2{=}CH_2}$$

$$\sim CH_2CH_2OCH_2OCH_2CH_2SS\sim$$
$$\downarrow$$
$$\sim CH_2CH_2OCH_2OCH_2CH_2\dot{S} + \dot{S}\sim$$
$$\downarrow$$

$\underline{H_2S}$ + unidentified destruction products.

The fact that polysulfide rubbers destruction takes place forming an intermediate substance having the character of free radicals is confirmed by EPR data from which it follows that the concentration of these radicals (Figure 6) increases with heating time enhancement, at thermolysis temperature 257°C, and are most probably radicals of the —R—S type.

Thus, the investigation of thermal destruction of aliphatic polysulfide rubbers has shown that the main processes of their destruction is the radical rupture of the —S—S— bonds followed by depolymerization.

However, the depth of this process depend on the polymer structure. The least thermally resistant proved to be rubber I.

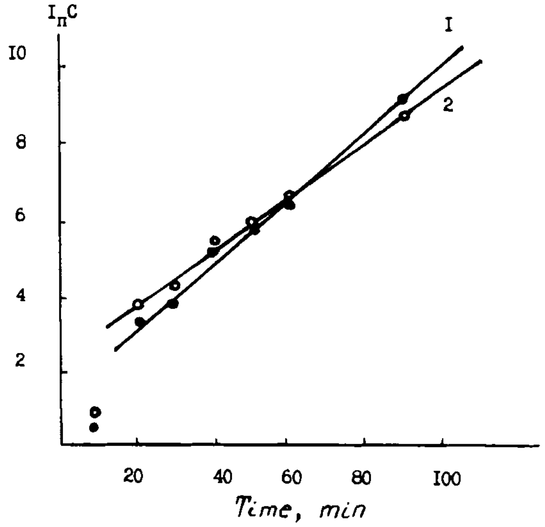


FIGURE 6 Logarithm of free radicals concentration vs. heating time at 257°C as exemplified by polysulfide rubbers: 1—I and 2—III.

The modification of polysulfide I leads to a certain increase in the temperature at the destruction onset (polymers II–IV). The introduction of aromatic fragments enhances especially the thermal resistance of the polymers.

The possible reason for the enhancement of the thermal resistance via polymer I modification is the discontinuity of the depolymerization chain on the —CH_2CH_2SS-groups, cross-links (polymer II) and aromatic fragments (polymer IV).[12-14]

The tentative evaluation of the thermal-oxidative stability of the polysulfide rubbers was derived from the thermogravometric curves taken in the air at a temperature rising rate of 5°C/min. According to the TGA data (Figure 7), it follows that the onset of polysulfide destruction occurs at 200°C, whereas at 300°C they decompose already 70–80%, the destruction process proceeding with a minor heat effect. This allows us to conclude that the weight loss occurs not by the oxidatory processes, but by the depolymerization and volatility of the low-molecular destruction products.

A further slow decrease in weight takes place in the temperature range 300–600°C. This decrease is also accompanied by a small exothermal effect with the exception of polymer IV whereas this stage proceeds with a considerable evolution of heat.

The thermal oxidation of rubbers carried out in ampouled under oxygen pressure 150 mm Hg (which comprises 2 moles of O_2 per polymer link) has shown that at low temperature (140–160°C), the rubbers are resistant to oxidation over a long period of time, yet they lose considerable weight.

The next figure shows the kinetic weight lost curves due to polymers oxidation at 140°C for 40 h and at 160° for 20 h (Figure 8a and b).

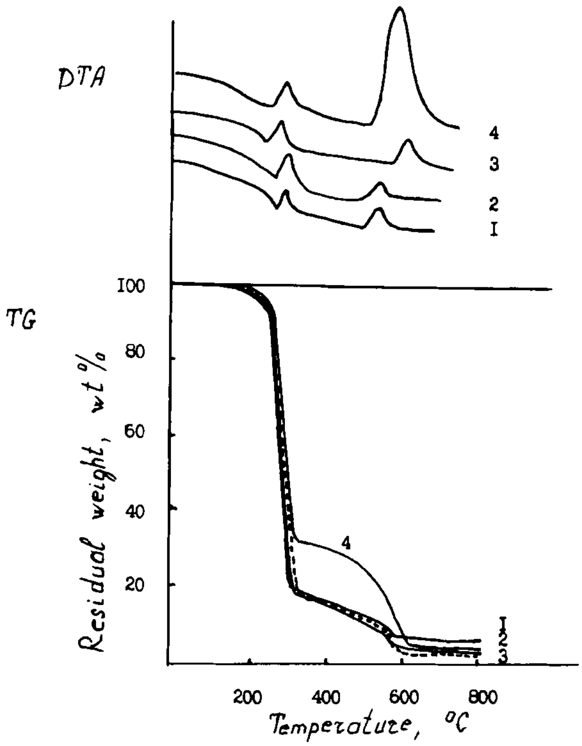


FIGURE 7 Thermogravometric curves for elastomer destruction of polysulfide exposed to air. Temperature rising rate—5 deg/min.

No oxygen absorption was observed at 140°C up to 5 h, but after 40 h, the absorption comprised 0.02–0.03 mole per polymer link.

At 160°C, only 0.05 mole of oxygen per polymer link was absorbed in the course of 20 h.

Acetaldehyde, traces of hydrogen sulfide and carbon oxysulfide were detected in the volatile destruction products, the liquid destruction product represents a cyclic monomer.

In connection with this, oxidation was carried out at high (210–250°C) temperatures for evaluating the comparative thermal-oxidative resistance of polysulfides of different structures.

Figure 9 shows the dependence of the amount of absorbed oxygen on the thermal-oxidative destruction temperature from which it follows that a greater amount of oxygen is absorbed by polymer I. At 250°C no thermal oxidation of polymer I could be carried out, because the ampoules blasted, perhaps due to the formation of the explosion-proof correlation between carbon oxysulfide and oxygen.

Carbon oxide, ethylene, hydrogen sulfide, carbon oxysulfide appeared to be the basic gaseous destruction products of the aromatic rubbers. At 250°C, sulfide gas was detected in small quantities (Table IV).

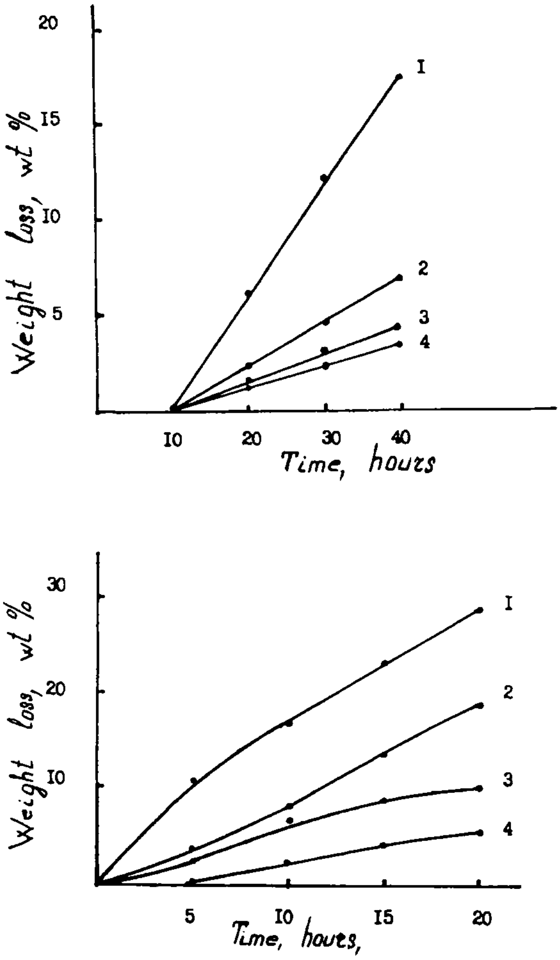


FIGURE 8 Kinetic curves for weight loss during thermal polysulfides oxidation: 1—I, 2—II, 3—III, 4—IV: a—at 140°C, b—at 160°C.

It should be noted that although the amount of gaseous products by oxidation compares favourably with that by thermal destruction, it is nevertheless also small in comparison with the amount of liquid products of polymer destruction.

The kinetic curves for the rubber oxidation at 210, 225, 235°C over a period of 120 min have shown that oxygen absorption takes place with an induction period and assumes an S-shape character. The kinetic curves for the oxygen absorption are examplified in Figure 10. The same dependences were obtained also for temperatures of 210 and 235°C.

The induction period is also noticeable on the kinetic curves of gaseous products formation, whilst the kinetic dependences of liquid products isolation do not have an induction period.

This experimental fact indicates that the formation of polymer destruction

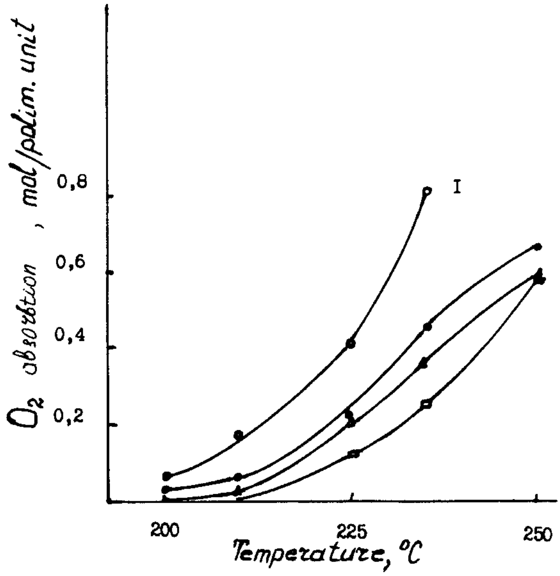


FIGURE 9 Absorbed oxygen quantity vs. destruction temperature for polysulfides: 1—II, 2—II, 3—III, 4—IV.

TABLE IV

Composition of polysulfide rubber destruction products in an atmosphere of 2.5 mole oxygen on the elementary polymer link during 1 hour heating at each temperature

Polymer number	Destruct. temp. °C	Amount of O_2 abs., mole/bas. mol	Total weight loss, wt%	Gas degradation products, mole/basically mole					
				C_2H_2	H_2S	COS	SO_2	CO	CO_2
I	200	0.07	16.6	traces	—	—	—	0.02	0.01
	210	0.18	24.2	0.02	traces	traces	—	0.02	0.02
	225	0.40	31.3	0.05	0.04	0.03	traces	0.14	0.08
	235	0.81	68.6	0.12	traces	0.05	0.03	0.22	0.15
II	200	0.04	9.0	traces	traces	—	—	—	—
	210	0.07	15.6	traces	traces	traces	—	traces	traces
	225	0.21	37.5	0.03	0.11	0.03	—	0.05	0.06
	235	0.45	71.7	0.07	0.06	0.06	traces	0.13	0.14
	250	0.66	70.5	0.09	0.07	0.08	0.034	0.21	0.15
III	200	—	7.2	traces	traces	—	—	—	traces
	210	0.04	15.2	traces	0.01	traces	—	—	traces
	225	0.12	37.0	0.03	0.11	0.02	—	0.03	0.01
	235	0.35	70.6	0.04	0.28	0.06	—	0.08	0.12
	250	0.60	70.4	0.08	0.18	0.06	traces	0.11	0.11
IV	200	—	2.5	—	traces	—	—	—	—
	210	—	7.5	—	0.02	traces	—	—	—
	225	0.12	31.6	0.02	0.23	0.03	—	0.02	0.04
	235	0.25	42.9	0.04	0.34	0.06	—	0.08	0.11
	250	0.60	48.3	0.09	0.18	0.08	traces	0.15	0.16

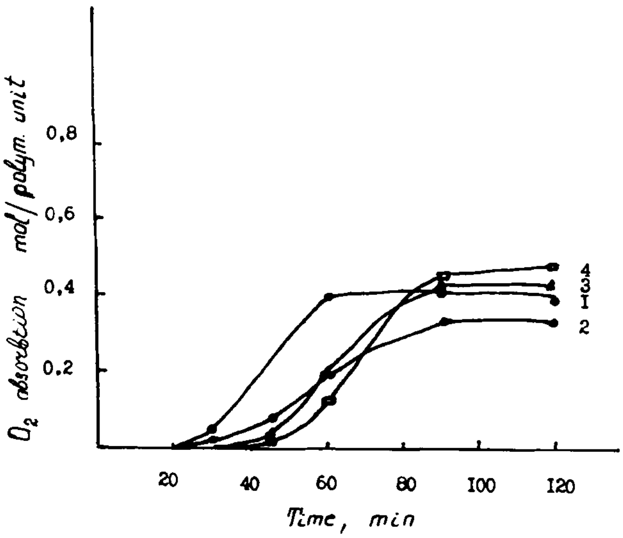


FIGURE 10 Kinetic curves for oxygen absorption by aliphatic polysulfides: 1—I, 2—II, 3—III, 4—IV at 225°C.

products occurs at the expense of secondary reactions and include destruction products formed at the first stage.

The number of oxides of carbon, ethylene, carbon oxysulfide increases with increasing heating time, whilst the dependence of hydrogen sulfide evolution has a complicated character.

From the data of Figure 11 which presents the kinetic curves of hydrogen sulfide evolution at 235°C, it follows that H_2S decreases gradually with time. This is likely due to the fact that the gas-phase reactions between the hydrogen sulfide

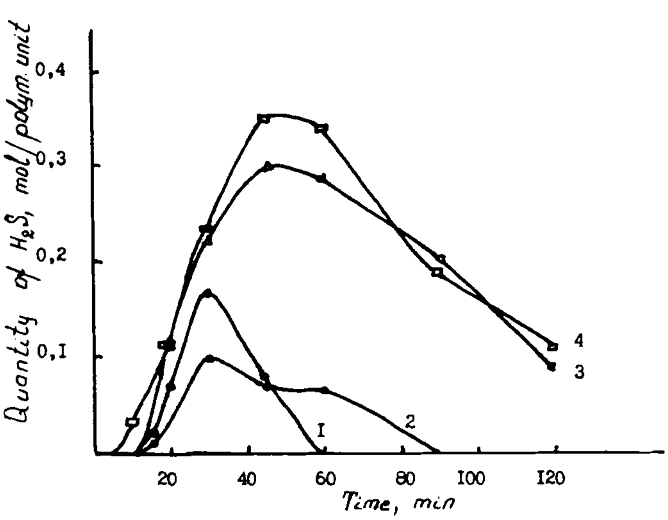
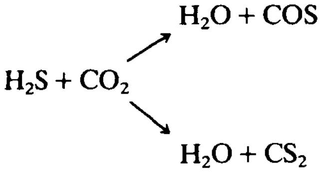


FIGURE 11 Kinetic curves for hydrogen sulfide evolution during rubbers oxidation: 1—I, 2—II, 3—III, 4—IV at 235°C.

and carbon dioxide proceeds by the following scheme:[15]

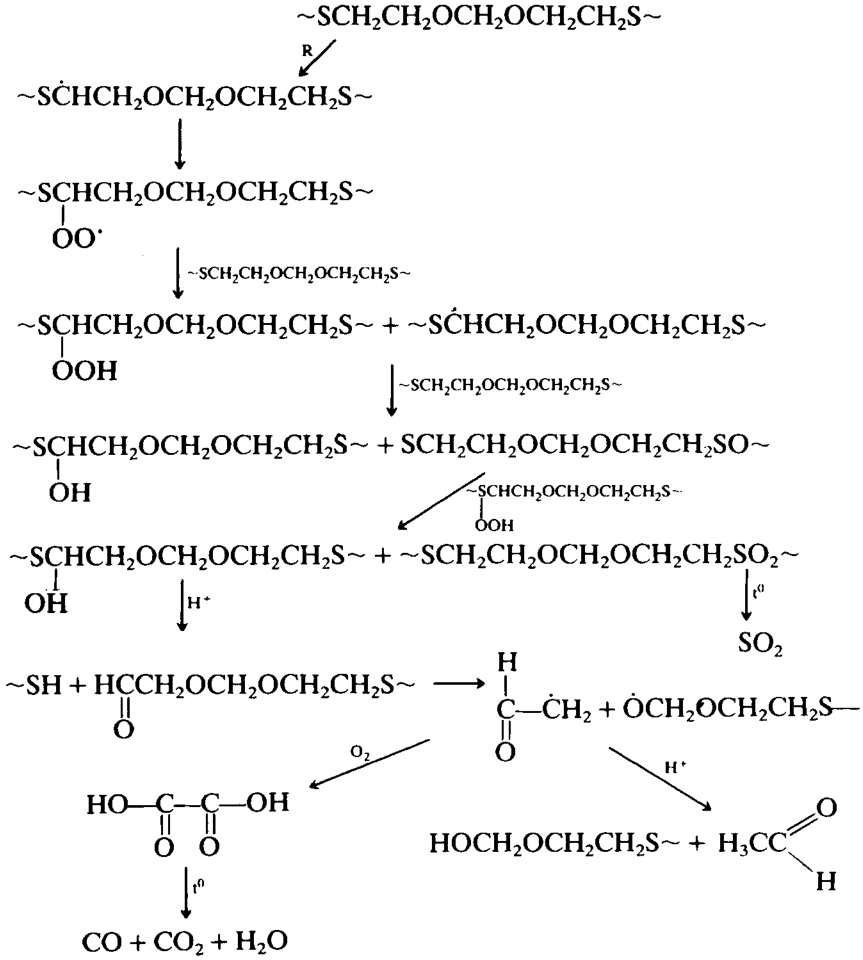


Possibly, such a reaction occurs also in vacuum, however, due to the small amount of CO_2 in the thermal destruction products, we failed to observe a decrease in H_2S with time.

The decrease in H_2S with time during thremal oxidation of the rubbers may also occur through the reaction:[16]

$$H_2S + \tfrac{1}{2}O_2 \rightarrow H_2O + S$$

On the basis of the investigation carries out and taking into account the literature data on aliphatic polymers,[17,18] we may assume that the oxidation of rubbers proceeds according to the following scheme:



At high temperature, alongside with the oxidation of the polymer, depolymerization takes place rather intensively to form cyclic products which also undergo oxidation. The presence of the induction period on the kinetic curves of evolution of oxidation products and the absorption of oxygen is probably also related to the circumstance that the oxidation of the cyclic occurs more readily than in the case of the polymer.

On the basis of the experimental data obtained, we may conclude that in the case of thermal destruction, polymer IV is more resistant to oxidation, whilst less resistant is polymer I.

References

1. E. Tchaushesku, *Recent Investigation of High-Molecular Compounds.* M.: Khimiya, 1981, p. 178.
2. L. Bellamy, *Infrared Spectra of Complex Molecules.* M.: I.L. 1963, p. 220.
3. E. H. Catsiff, M. N. Gillis and R. H. Gorban, *J. Polym. Sci.*, **A1, 9,** 1271 (1971).
4. Thioplast Leipzig, 1971, p. 89.
5. E. R. Bertozzi, *Rubber Chem. Technol.*, **41,** 114 (1968).
6. F. O. Davis and E. M. Fettes, *J. Am. Chem. Soc.*, **70,** 2611 (1948).
7. A. V. Tobolsky and G. P. Leonard, Poeser, *J. Polym. Sci.*, **3,** 604 (1948).
8. L. Bellamy, *Infrared Spectra of Complex Molecules.* M.: I.L., 1963, p. 497.
9. K. B. Piotrovsky. In: *Aging and Stabilization of Polymers.* Ed. A. S. Kusuminsky, M.: Khimiya, 1966, p. 104.
10. W. Waters, *Mechanism of Oxidation of Organic Compounds.* M.: MIR, 1966, p. 15.
11. N. Grassy, *Chemistry of Polymer Destruction Processes.* M.: I.L., 1959, p. 187.
12. K. A. Andrianov, G. I. Pashintseva, S. R. Nanym'yan and V. V. Severnyi, *Vysokomolec. soyed. A*, **15,** N8, 1809 (1973).
13. S. B. Dolgoplosk, *Vysokomolec. soyed.*, *A*, **12,** N10, 2238 (1970).
14. K. A. Andrianov, A. I. Nogaideli and I. zv. Tkeshelashvili, *AN SSSR, ser. khim.*, N3, 515 (1972).
15. G. Remi, *Course of Inorganic Chemistry.* M.: Mir, 1972, p. 448.
16. G. Remi, *Course of Inorganic Chemistry.* M.: Mir, 1972, p. 703.
17. B. M. Kovarskaya, *Zh. VKhD*, **11,** N5, 261 (1966).
18. M. N. Gillis, E. H. Catsiff and R. H. Gobran, *J. Polym. Sci.*, **A1, 9,** 1293 (1971).