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Citation: *J. Chem. Phys.* **14**, 93 (1946); doi: 10.1063/1.1724110

View online: <http://dx.doi.org/10.1063/1.1724110>

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## Stress-Time-Temperature Relations in Polysulfide Rubbers

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(Received November 14, 1945)

Polysulfide rubbers of various internal structures have been investigated by measurements of continuous and intermittent relaxation of stress and by creep under constant load at temperatures between 35°C and 120°C. Continuous stress relaxation measurements indicate that these rubbers approximately obey the simple Maxwellian law of relaxation of stress, which indicates that one definite type of bond in the network structure is responsible for stress decay. The activation energy for the relaxation process in each of the polysulfide rubbers is nearly the same, indicating that the same type of bond is responsible

for the relaxation behavior of all the polysulfides investigated. In contrast to the hydrocarbon rubbers, oxygen is not the cause of high temperature relaxation in polysulfide rubbers, nor does heating in air at moderate temperatures for times comparable to the relaxation time produce changes in physical properties as determined by modulus or by appearance of the samples. Several possibilities regarding the mechanism of the relaxation process and the type of bond involved are considered in the light of the experimental results.

**M**EASUREMENT of relaxation of stress for various hydrocarbon rubbers has been used to investigate the relationships between the physical and structural-chemical characteristics of these materials.<sup>1</sup> The present investigation is an extension of these studies to the polysulfide rubbers.

The structures of rubber-like materials have been considered to be three-dimensional networks constructed from long chain molecules linked at infrequent points. The point where two chains are linked is referred to as a network juncture, and the portion of the long polymer molecule between two junctures is referred to as a network chain. In the unstrained state the network chains tend to assume randomly coiled configurations, the degree of randomness being limited by steric considerations and by interactions with neighboring chains. In the stretched state the network chains of the rubber are forcibly uncoiled, and the stress is calculated from probability considerations in the kinetic theory of elasticity<sup>2</sup> by the equation

$$f = skT \left[ \left( \frac{l}{l_u} \right)^2 - \frac{l_u}{l} \right], \quad (1)$$

where  $f$  = stress on attained section,  $s$  is the number of strained elements (network chains) of

the structure per unit volume,  $kT$  is the thermal energy, and  $l/l_u$  is the ratio of stretched to unstretched length.

The network structure must be regarded as a dynamic structure. Strained elements tend to relax their strain because of slippage or rupture at the network junctures or by scission or rupture along the chains. On the other hand, new structural elements (network chains) are always being formed by reformation of bonds or by the formation of new bonds between the chains.

In previous papers<sup>1</sup> it was argued that bond reformation or cross-linking occurs in general in such a way that the network elements thereby formed are relaxed at the moment of formation and do not contribute to the stress in any configuration of the rubber at which they are formed unless the sample is further strained. For this reason studies of the decay of stress at constant extension isolate the various processes of interchain slippage or rupture at juncture points and/or bond scission along the network chains. On the other hand, occasional and momentary measurements of the stress required to attain a definite extension, the sample being maintained in an unstrained state between measurements, provide a means of measuring the net rate of bond breakage plus bond reformation through Eq. (1). These experiments are referred to as continuous relaxation of stress measurements and intermittent relaxation of stress measurements, respectively. The techniques of these measurements have been previously described.

<sup>1</sup> A. V. Tobolsky, I. B. Prettyman, and J. H. Dillon, *J. App. Phys.* **15**, 380 (1944); A. V. Tobolsky and R. D. Andrews, *J. Chem. Phys.* **13**, 3 (1945).

<sup>2</sup> E. Guth and H. M. James, *J. Chem. Phys.* **11**, 455 (1943); F. T. Wall, *J. Chem. Phys.* **10**, 132 (1942); **10**, 485 (1942); L. R. G. Treloar, *Trans. Faraday Soc.* **40**, 59 (1944); P. J. Flory, *Chem. Rev.* **35**, 51 (1944).

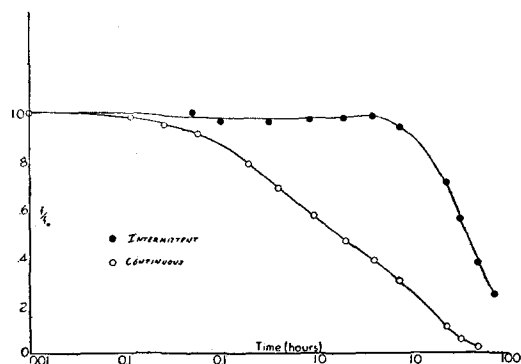


FIG. 1. Continuous and intermittent stress relaxation of Butyl rubber: 130°C, 50 percent elongation. ○ continuous, ● intermittent.

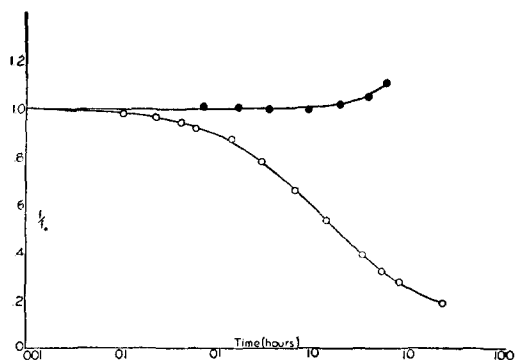


FIG. 2. Continuous and intermittent stress relaxation of Butaprene NM: 130°C, 50 percent elongation. ○ continuous, ● intermittent.

Figures 1 and 2 show intermittent and continuous relaxation of stress data at 130°C for Butyl (polyisobutylene-isoprene) rubber and for Butaprene NM (butadiene-acrylonitrile) rubber, respectively, the data being plotted as stress divided by initial stress against logarithmic time. These gum vulcanizates have been described in a previous paper.<sup>1</sup> It is apparent from these data that processes of bond scission and bond formation (or cross linking) are occurring simultaneously in both of these vulcanizates. In the case of Butyl rubber, scission is more rapid since the intermittent curve shows stress decay, whereas in Butaprene NM cross-linking predominates because the intermittent curve shows a stress rise. Both scission and cross-linking are caused by the presence of molecular oxygen.

Figure 3 shows similar data for H-11 at 60°C. It is apparent that, inasmuch as the intermittent curve is perfectly flat, the rates of bond breaking

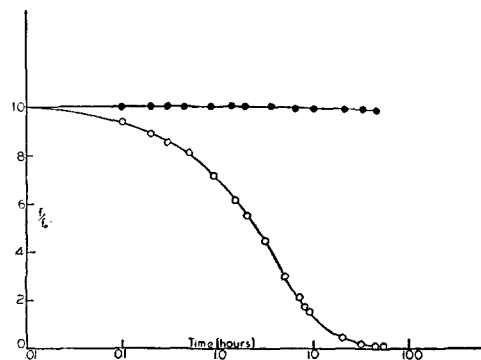


FIG. 3. Continuous and intermittent stress relaxation of H-11: 60°C, 50 percent elongation. ○ continuous, ● intermittent.

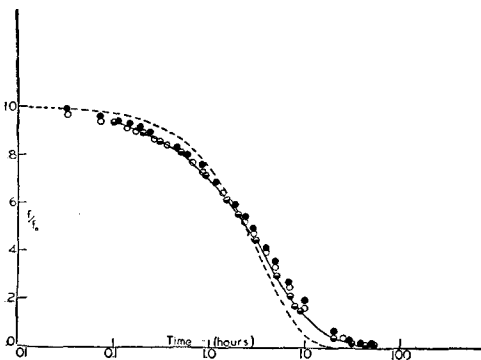


FIG. 4. Continuous stress relaxation of H-11 at various elongations, and plot of  $\exp(-k't)$  at 60°C. -----  $\exp(-k't)$ , ● 10 percent elongation, ○ 30 percent, ◐ 50 percent.

and bond formation are exactly equal. This is generally true for all the polysulfide rubbers studied over a wide range of temperature. Furthermore, the bond breaking reaction appears independent of the presence of molecular oxygen from experiments run in high vacuum. From Fig. 3 it is apparent that heating in air for times comparable to the relaxation time produces no change in modulus, nor are any other physical or chemical changes observable on visual and manual inspection. Finally, the initial stress required to attain 50 percent elongation was found not to vary appreciably over a wide temperature range. For example, for H-11, the initial stress required to attain 50 percent elongation over a range of temperatures from 30 to 100°C did not vary by more than 1 percent, which is within the limits of experimental error.

Figure 4 shows the continuous stress relaxation curves of H-11 at 10 percent, 30 percent, and

50 percent extension and at 60°C with stress divided by initial stress being plotted against logarithmic time. A dashed curve representing a plot of  $\exp(-k't)$  versus log time is also shown where  $k'$  has been chosen to give the best fit of the experimental relaxation data. It is apparent that the effect of elongation on these relaxation curves is very small in this range of elongation, and that the experimental curves closely obey the law

$$f/f_0 = e^{-k't}. \quad (2)$$

It follows from Eq. (1) that the rate of stress relaxation caused by slippage at the network junctures or by rupture of bonds along the chain is given by

$$-(1/s)(ds/dt) = k', \quad (3)$$

where  $k'$  may contain, as a multiplicative factor, the number of bonds along the chain susceptible to scission. This simple stress decay law indicates that a single type of bond (with one single rate constant) is responsible for relaxation.

#### CREEP UNDER CONSTANT LOAD

The behavior of H-11 (which is representative of all the polysulfide rubbers studied) as exemplified in Figs. 3 and 4 would appear to indicate that we were dealing with an almost perfect Maxwellian body which obeyed Maxwell's law

$$ds/dt = (1/G)(df/dt) + (k'f/G), \quad (4)$$

where  $ds/dt$  is rate of strain,  $f$  is stress,  $G$  is an

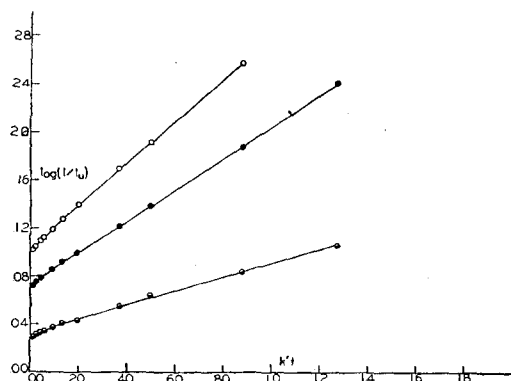


FIG. 5. Creep curves of H-7 at 60°C.  $l$ =extended length at time  $t$ ,  $l_u$ =unextended length,  $l_0$ =initial extended length;  $k'$  is obtained from stress relaxation data at 60°C.  $\log_{10}$  vs.  $k't$ ,  $\circ$   $l_0$ =25.1 percent,  $\bullet$   $l_0$ =16.9 percent,  $\ominus$   $l_0$ =6.5 percent.

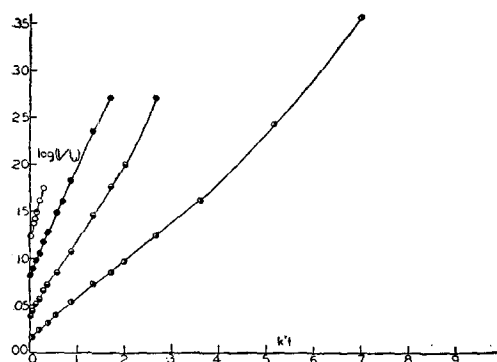


FIG. 6. Creep curves of H-11 at 60°C.  $l$ =extended length at time  $t$ ,  $l_u$ =unextended length,  $l_0$ =initial extended length;  $k'$ =rate constant obtained from stress relaxation data at 60°C.  $\log_{10}$  vs.  $k't$ ,  $\circ$   $l_0$ =32.8 percent,  $\bullet$   $l_0$ =20.8 percent,  $\ominus$   $l_0$ =9.4 percent,  $\bullet$   $l_0$ =3.2 percent.

elastic modulus, and  $k'$  a relaxation rate. Equation (4) would quantitatively explain the results shown in Figs. 3 and 4 and Eq. (2). However, since Eq. (1) indicates that the elastic stress-strain law is not linear (non-Hookean spring) it is clear that Eq. (4) could not be an exact representation of all the elastic viscous behavior of polysulfide rubbers, even were we to overlook the slight disparity in the fit of the relaxation curve to  $e^{-k't}$ . Results on creep, obtained by a previously described method,<sup>3</sup> bear this statement out very strikingly. Whereas the Maxwell Eq. (4) would predict a linear creep with time, the experimental data (Figs. 5 and 6) indicate a creep whose time dependence is even stronger than exponential. This cannot be accounted for in terms of changing cross section alone, but rather must be interpreted in terms of Eq. (1). A complete discussion of the theory of creep will appear in an accompanying article.

Observations were also made on the mechanical behavior after removal of load during creep experiments. An initial rapid contraction followed by a small, slow creep recovery was noticed. If we had a system that could be strictly characterized by one reaction rate, as in Eq. (2), we could expect no creep recovery. Actually about 5 percent recovery is observed which isn't surprising in view of the slight deviation from  $e^{-k't}$  evinced in Fig. 4.

The theory previously derived which appar-

<sup>3</sup> R. D. Andrews, R. B. Mesrobian, and A. V. Tobolsky, Trans. A.S.M.E. 67, 569 (1945).

TABLE I.

64H	H3	H5	H8	H9	H10	H11	H12
Organic tetrasulfide	100	—	—	—	—	—	—
Organic tetrasulfide	—	100	—	—	—	—	—
Organic disulfide cross-linked	—	—	100	—	—	—	—
Organic disulfide	—	—	—	100	—	—	—
Organic disulfide tetrafunctional	—	—	—	—	100	—	—
Organic disulfide	—	—	—	—	—	100	—
Organic disulfide with 40% monosulfide	—	—	—	—	—	—	100
Zinc oxide	10	10	—	—	—	10	—
Pelletex	—	60	60	60	60	60	60
Micronex	25	—	—	—	—	—	—
Stearic acid	.50	.50	.50	1.00	1.00	.50	1.00
Altax	—	—	—	—	—	.30	—
DPG	.10	—	—	—	—	.10	—
Tuads	.25	.25	—	—	—	—	—
Lead peroxide	—	—	1.50	1.50	1.50	—	1.50
Cure	50×287	30×287	30×287	30×287	30×287	50×298	30×287
Modulus 100	—	—	540	310	450	515	340
300	—	—	—	1200	1475	1185	—
500	—	—	—	—	—	—	—
Tensile	730	450	1160	1520	1475	1185	985
Elongation	370	400	190	420	300	300	280
Set	—	—	2	5	3	10	5
Hardness	74	70	73	68	74	76	64

ently satisfactorily explains the creep of Butyl and Hevea rubbers at elevated temperatures is strictly true only in the case that there is a scission reaction only. The satisfactory agreement for Butyl and Hevea occurs because in these rubbers the scission reaction predominates. This theory does not apply, nor can it be expected to apply, to the polysulfide rubbers where the rate of bond formation in the network structure is equal to the rate of bond breaking.

#### RELAXATION STUDIES OF VARIOUS POLYSULFIDE RUBBERS OVER A RANGE OF TEMPERATURE

In order to obtain some further insight into the nature of bonds whose rupture is responsible for the relaxation of stress in the polysulfide rubbers, a series of these rubbers prepared for us by the Thiokol Company were studied over a range of temperatures. The rubbers studied included two tetrasulfide polymers H-3 and H-5, two linear disulfides, a disulfide containing a fairly large percentage of monosulfide linkages, one disulfide containing two percent of trifunctional agent, and one disulfide containing one percent of tetrafunctional agent. Table I details these polymers and the compounding and curing recipe for the rubbers obtained therefrom. The relaxation curves for all these rubbers at 60°C

is shown in Fig. 7. It is apparent that the relaxation rate varies by a factor of about one thousand from the fastest to the slowest of these compounds. The tetrasulfides relax the most rapidly; the inclusion of polyfunctional agents apparently slightly retards the rate of relaxation.

The temperature dependence of the relaxation rates for these rubbers is shown in Figs. 8-14. In these graphs, stress divided by initial stress is plotted against logarithmic time for a series of different temperatures. Inasmuch as all the decay curves are approximated by the decay law  $e^{-k't}$ , a very simple method for obtaining the activation energies for stress decay was employed. As shown in Fig. 8 a horizontal line was drawn across the graphs at a value of  $f/f_0 = .368 = 1/e$ . The intersection of this horizontal line with the decay curves at the various temperatures gives the time for which  $k' = 1/t$ . Since in these curves time is already plotted on a logarithmic scale, a scale of reciprocal absolute temperature is plotted on the right-hand side of the figures along the ordinate scale. By locating the time for which  $t = 1/k'$  against the corresponding temperature on the reciprocal temperature scale, a plot of  $\log 1/k'$  vs.  $1/T$  is obtained. The figures indicate that straight lines are obtained for all the rubbers studied and the slopes

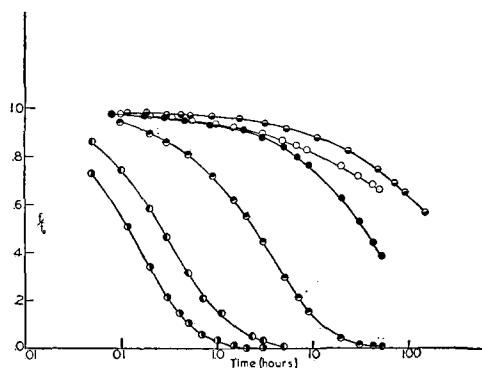


FIG. 7. Continuous stress relaxation of various polysulfide rubbers at 60°C, 50 percent elongation. ● H-10, ○ H-2, ● H-7, ● H-11, ● H-3, ● H-5. (See Table I.)

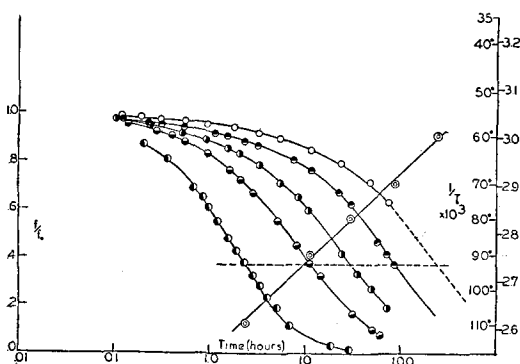


FIG. 10. Continuous stress relaxation of H-8 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ . ○ 60°C, ● 70°C, ● 80°C, ● 90°C, ● 110°C.

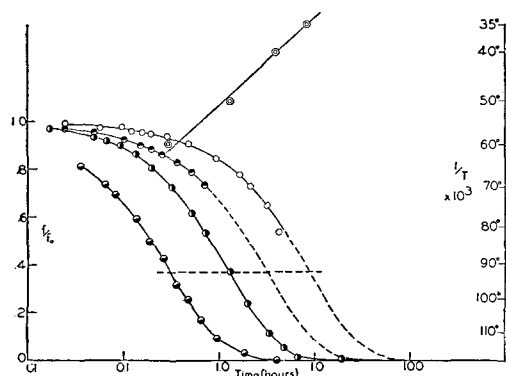


FIG. 8. Continuous stress relaxation of H-3 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ . ○ 35°C, ● 40°C, ● 50°C, ● 60°C.

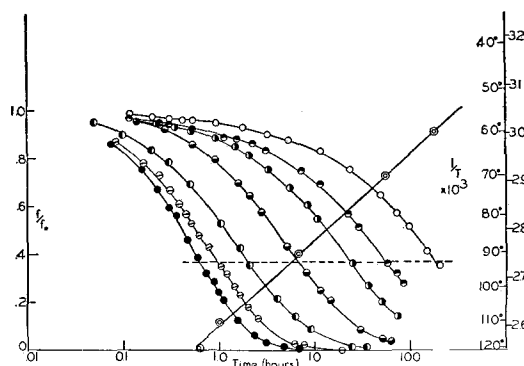


FIG. 11. Continuous stress relaxation of H-9 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ . ○ 60°C, ● 70°C, ● 80°C, ● 90°C, ● 100°C, ● 110°C, ● 120°C.

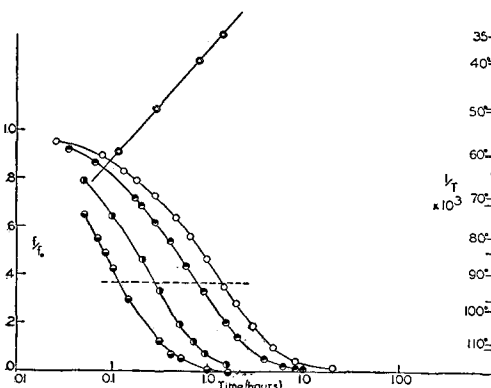


FIG. 9. Continuous stress relaxation of H-5 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ . ○ 35°C, ● 40°C, ● 50°C, ● 60°C.

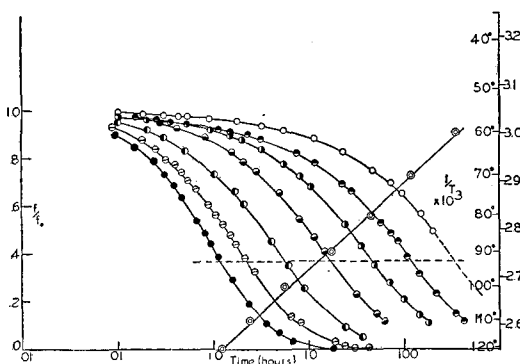


FIG. 12. Continuous stress relaxation of H-10 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ . ○ 60°C, ● 70°C, ● 80°C, ● 90°C, ● 100°C, ● 110°C, ● 120°C.

of the straight lines give a measure of the heat of activation. The heats of activation for the various rubbers are tabulated in Table II as are the entropies of activation. It is clear that

although the absolute values of the relaxation rates are very different (see Fig. 7), the heats of activation for all the polysulfide rubbers do not differ markedly.

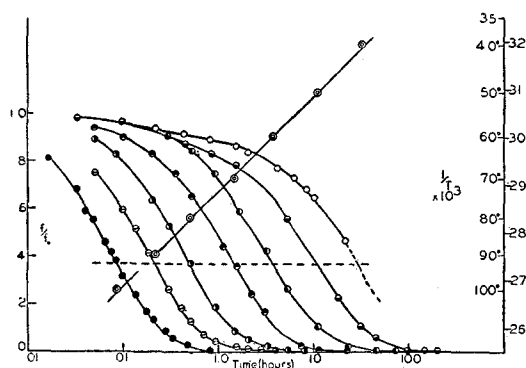


FIG. 13. Continuous stress relaxation of H-11 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ .  $\circ$  40°C,  $\bullet$  50°C,  $\bullet$  60°C,  $\bullet$  70°C,  $\bullet$  80°C,  $\bullet$  90°C,  $\bullet$  100°C.

A pair of curves suffices to present the complete stress-time-temperature relations for a given rubber. For example, Fig. 15 shows how this can be done for H-11. A "universal stress-decay curve" is plotted against  $\log k't$  inasmuch as the decay curves are approximately superposable by translation along the logarithmic time axis. A plot of  $\log k'$  against  $1/T$  is shown on the same figure where the same logarithmic scale is used as abscissa, and the  $1/T$  scale is plotted as the ordinate scale on the right-hand side of the figure. The values of  $k'$  at any temperature for this graph can be readily obtained from Fig. 13 by taking the reciprocal of the time at the given temperature at which the value of  $f/f_0 = e^{-1}$ . Figure 15 may now be used to give the complete stress-time behavior for relaxation at any temperature. The log-time scale at any temperature always has the spacing shown along the abscissa and may be located along the abscissa by using the straight-line locus of  $\log k'$  vs.  $1/T$ .

### DISCUSSION

The simple relaxation behavior (given by Eq. (2)) of any single polysulfide rubber studied here is strong evidence that a single type of bond in the structure is involved. Furthermore, the approximate equality of the energy of activation for stress decay in all the polysulfide rubbers is an indication that the relaxing bond is in each case closely similar, perhaps identical, even in the case of the disulfides and tetrasulfides. Moreover, the facts indicate that the total num-

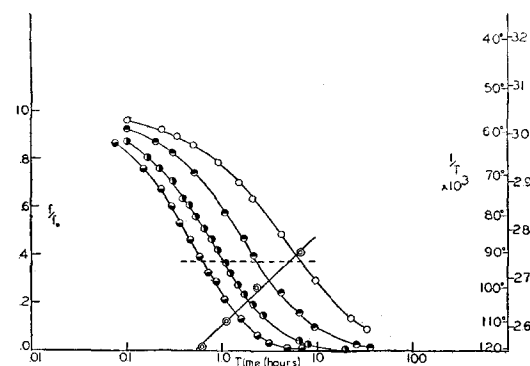


FIG. 14. Continuous stress relaxation of H-12 at various temperatures and 50 percent elongation; plot of  $\log k'$  vs.  $1/T$ .  $\circ$  90°C,  $\bullet$  100°C,  $\bullet$  110°C,  $\bullet$  120°C.

ber of structural elements does not change with time or temperature, so that the bonds involved reform at exactly the same rate that they break and the equilibrium between breaking and reforming of bonds does not change with temperature.

It is not possible to make a final decision at this point as to precisely which bond of the structure is responsible for relaxation. It is conceivable that a primary chemical bond along the chain is breaking and reforming, possibly by the simple expedient of bond interchange between two chains. On the other hand, it is also possible that the cross-linking bond between chains is in fact responsible for the thermoplastic behavior. It was hoped that the use of tetrafunctional and trifunctional cross-linking agents would provide a means of tying the molecules into a three-dimensional structure. If these cross-linked polymers showed a limited relaxation instead of a complete relaxation to zero stress, it would be possible to state unequivocally that the relaxation in the linear disulfides and tetrasulfides was due to a slippage of interchain bonds. On the other hand, there is no conclusive evidence that the tetra and trifunctional agents

TABLE II.

Polymer	$\Delta H^\ddagger$ (kcal.)	$\Delta S^\ddagger$ (cal.)
H-3	25.41	+3.3
H-5	20.24	-10.0
H-8	24.28	-13.1
H-9	25.70	-8.2
H-10	25.08	-11.5
H-11	22.92	-8.9
H-12	24.47	-11.5

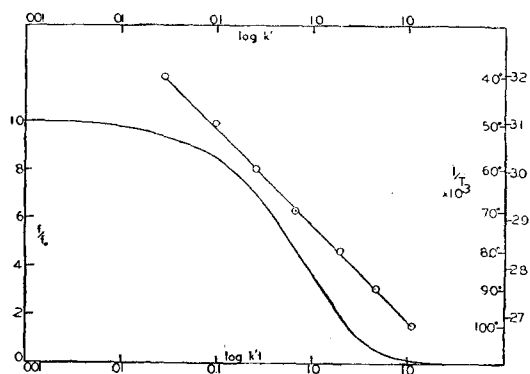


FIG. 15. "Universal curve" of H-11 and plot of  $\log k'$  vs.  $1/T$ .

used actually produce three-dimensional structures.

Considerations of the various possibilities put reasonable limits to the types of bonds responsible for polysulfide behavior. There are at least three bonds along the network chains, any one of which may be responsible for the observed phenomena. Whatever the bond, it must (1) have a low activation energy, (2) be formed as rapidly as it is broken throughout the temperature range, 35°–120°C, and (3) be insensitive to whether it is heated in vacuum or air. The three bonds along the polysulfide network chains are the C–C, C–S, and S–S bonds. Pauling<sup>4</sup> gives the C–C bond energy (per mole) as 58.6 kcal., the C–S as 54.5 kcal., and the S–S bond energy as 63.8 kcal. The C–S bond thus appears to be the weakest and the S–S bond the strongest of the three.

The experiments on creep in vacuum and stress relaxation in oxygen-free nitrogen indicate that the relaxation behaviors of the hydrocarbon rubbers are due to oxidative attack, since the rate of scission is decreased a thousandfold in vacuum at  $10^{-5}$ -mm pressure.\* Experiments on relaxation of polysulfide rubbers in vacuum at  $10^{-5}$ -mm pressure indicate that oxygen is not responsible for their relaxation behavior (Fig. 16). On the other hand, temperature does appear to have a primary effect on the relaxation rates of polysulfides both in vacuum and air as contrasted to its secondary effect on hydrocarbon rubbers in vacuum.\* Furthermore, the  $\Delta H^\ddagger$  of

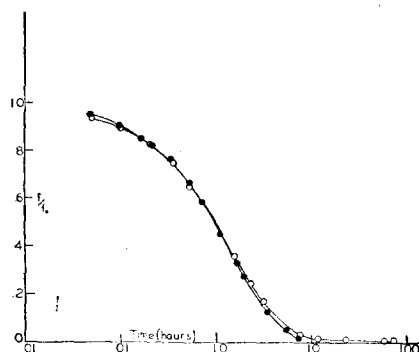


FIG. 16. Continuous stress relaxation of H-11 in vacuum and air at 70°C, 50 percent elongation. ○ Air, ● Vacuum.

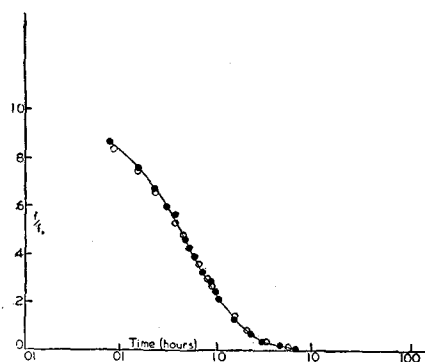


FIG. 17. Continuous stress relaxation of H-9 and H-12 at 120°C, 50 percent elongation. ● H-9 (disulfide), ○ H-12 (monosulfide and disulfide).

hydrocarbon rubbers of  $30.4 \pm 2.0$  kcal. as contrasted to the  $\Delta H^\ddagger$  of  $24 \pm 1.5$  kcal. in polysulfides indicate that essentially one type of chemical reaction involving very similar chemical bonds is responsible for the relaxation behavior of all the hydrocarbon rubbers and that this reaction is not the same as the one responsible for polysulfide behavior. Thus it appears reasonable to assume that the hydrocarbon portion of the structure is not responsible for polysulfide behavior, although the possibility does exist that a C–C bond adjacent to a sulfur atom in a network chain may be sufficiently weakened by the presence of the sulfur atom as to satisfy the conditions stated above. The accessibility of *d*-orbitals in sulfur to partial double-bond formation makes such a weakening of adjacent C–C bonds possible, and poses a problem for further research.

<sup>4</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939.)

\* Unpublished experiments of W. C. Scheider and M. Magat and also unpublished work of present authors.

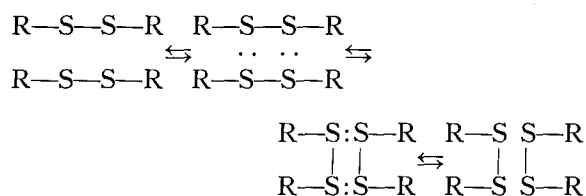


The relaxation experiments on H-12, a rubber consisting of both monosulfide and disulfide links along the network chains, indicate that there is little difference in its relaxation rate from that of a disulfide polymer (Fig. 17). The fact that there is little difference in the relaxation rates of the two rubbers indicates that the C—S bond is at least as strong, if not stronger, than the S—S bond. Furthermore, as pointed out in Gilman,<sup>5</sup> the formation of monosulfides (the C—S bond) from mercaptans occurs at high temperatures in the presence of catalysts such as metallic sulfides; the hydrogen attached to the  $\alpha$ -carbon in monosulfides is more acidic than in corresponding ethers (pointing up the tendency of sulfur to expand its valence shell due to the accessibility of its  $d$ -orbitals, producing partial double bonds,<sup>6</sup> thus strengthening the C—S bond and weakening the C—H bond on the  $\alpha$ -carbon); organic monosulfides do not react readily with elementary sulfur to form higher sulfides, whereas disulfides, trisulfides, and tetrasulfides readily add sulfur to form higher sulfides; conversely di and trisulfides may also be readily formed from higher sulfides by distillation. All these facts indicate that the S—S bond is more labile and less stable than the C—S bond, in contrast to their respective bond energies as given by Pauling. A further instance of this is provided by Powell and Eyring<sup>7</sup> who have indicated an S—S bond energy of  $27.5 \pm 5$  kcal. as compared with the Pauling value of 63.8 kcal.

In addition to bond scission along the primary valence chains of the polysulfide rubbers, it is also possible that relaxation is due to a slippage or rupture of bond between the polysulfide chains. It is not known at present whether the vulcanization process introduces primary cross links into the structure, and if so what the nature or energy of these cross bonds might be. It is conceivable that the cross linking in these rubbers is not due to the vulcanization process

but instead occurs through formation of relatively strong bonds between sulfur atoms in adjacent chains. These bonds, which may possibly involve the unshared electron in the sulfur valence shell, would be stronger than ordinary secondary bonds between chains, but weaker than most primary chemical bonds. The relaxation process may consist in the breaking and reformation of these interchain bonds.

The relaxation may also occur by a process of chain interchange to give two new chains which are chemically indistinguishable from the old ones and from each other. Such a process of chain interchange is illustrated below for the case of the disulfide linkage



A mechanism of this or similar type would account for all of our observed phenomena.

A final possibility exists, namely that some chemical agent introduced into the rubber in the emulsion or during compounding may be involved in breaking the polysulfide chains.

It is apparent that a complete identification of the bond responsible for relaxation in polysulfide rubbers would be of great interest, and that this identification will accompany an enhanced knowledge of the chemistry of mono and polysulfides.

#### ACKNOWLEDGMENTS

The authors wish to thank the Firestone Tire and Rubber Company and Princeton University for making possible our researches on the fundamental properties of high polymeric materials, and the Thiokol Corporation for contributing the Thiokol samples which made this particular investigation possible. In particular, we wish to thank Dr. Patrick, Dr. F. O. Davis, and Mr. E. Fettes of the Thiokol Corporation, and Dr. M. Mochulsky of Princeton, for the cooperation and useful advice they have rendered us.

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