

Studies of the network structure of rubber vulcanizates by cryoscopic methods: 2.

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The freezing point depression, ΔT , of swollen DCP-, TT- and sulphur-cured natural rubber in benzene was observed. The dependence of the parameter, a_H , introduced by Kuhn, was not affected by the type of structure of crosslink sites. It was found from the comparison of the experimental results and scaling law that a_H can reflect not only the difference in three-dimensional structure of network between a degraded and an undegraded rubber vulcanizates but also the difference in degraded network structures between rubber samples with various conditions of degradation.

(Keywords: freezing point depression; thermal degradation; scaling law, interchange reaction; rubber vulcanizates)

INTRODUCTION

A large freezing point depression by the swelling solvent in swollen gels (such as rubber vulcanizates) has previously been observed¹. The freezing point depression, ΔT , for swollen dicumene peroxide-cured natural rubber (DCP-cured NR) in benzene has been described in a previous paper². The parameter, a_H (introduced by Kuhn³) varies inversely with ΔT , and is closely correlated to the network chain density determined by the swelling method. In addition, a_H for degraded samples was always lower than that for nondegraded samples, even if both types of samples have similar network chain densities. For frozen gels in the swollen state, a_H is referred to as the parameter of 'crystal size'³. However, a_H should be regarded together with other experimental facts as an 'indication', which may be associated with the structure of the network, or gels^{2,4}.

Thus, it has been shown that a_H reflects not only the network chain density and the degree of degradation but also the difference in three-dimensional structure of network between a degraded and a non degraded rubber sample².

In order to give a_H physical meaning, the experimental results were expressed in terms of ξ by the following relationship²:

$$a_H \propto \xi^{2.00} \quad \text{for an nondegraded DCP-cured NR (1)}$$

$$a_H \propto \xi^{1.31} \quad \text{for a degraded DCP-cured NR in air(2)}$$

where, ξ is the screening length and corresponds to the root mean square distance between crosslinkages or entanglements in swollen gels⁵. Therefore, it is possible to discriminate between a degraded and a nondegraded network structure from the difference of the exponent in equations (1) and (2).

There has been a dispute for a long period of time about whether the scissions may occur along main chains or at

the crosslinkages in crosslinked polymers⁶. However, recent advances in chemorheology have elucidated the above problems⁷. Chemorheology has been used to show that the chain scission by thermo-oxidative degradation occurs randomly along the main chains. The thermal degradation of tetramethylthiuramdisulphide (TT) and sulphur-cured NR occurs by interchange reaction of polysulphides⁸ and by chain scission near the crosslink sites.

In this paper, the relationship between the exponent in equation (2) and degraded network structure by the different types of scission mechanism will be discussed in detail.

THEORETICAL BACKGROUND

The dependence of a_H on the concentration of polymer in swollen rubber vulcanizates at the equilibrium swelling, C_e , could be experimentally represented by²

$$a_H \propto C_e^{-B} \quad (B > 0) \quad (3)$$

where, B is a constant determined experimentally.

However, the relationship between ξ and C_e is given by⁵

$$\xi \propto C_e^{-3/4} \quad (4)$$

As the degradation of a network proceeds, the functionality generally decreases and the coefficient in equation (4) may be altered. The variations of the coefficient in equation (4) cannot be predicted by the scaling law when the functionality is decreased. Bastide modified the coefficient in equation (4) (which is applicable to a degraded network) by assuming that the radius of gyration of dangling chains (produced in degraded rubber vulcanizates) is approximately equal to that of star-shaped polymers with the same molecular weight as the dangling chains. This then enabled him to explain qualitatively his experimental data⁹. However,

the power law expressed by equation (4) is invariant and can apply not only to a nondegraded rubber vulcanizate but also to a degraded one⁹.

It is possible to derive the following relation from equations (3) and (4):

$$a_H \propto \xi^m \quad (m=4B/3) \quad (5)$$

(Equations (1) and (2) already described were derived using the above procedures).

EXPERIMENTAL

Natural rubber (NR; Pale crepe No. 1) was used in the present study. Uncrosslinked rubber was milled with curing ingredients under the conditions as described in Table 1. Sheets (~0.5 mm in thickness) of milled polymer were pressed at 2 MPa and 413~418 K for a given interval. The network chain densities of all samples are indicated in the last column of Table 1. All the samples were extracted by a hot azeotrope mixture of acetone (300 ml)/methanol (230 ml)/chloroform (470 ml) under nitrogen for 48 h and dried *in vacuo*. The crosslink sites of DCP-, TT- and sulphur-cured NR consist of carbon-carbon bonds, mono or disulphide bonds and polysulphide bonds, respectively⁷.

Degraded samples were immersed in benzene for 24 h at room temperature and dried *in vacuo*. The sample from which the soluble part of rubber (the sol) was removed was swollen in benzene for 24 h at 303 K. The equilibrium degree of swelling, Q , was determined from the increment of the weight of the swollen rubber sample, and the network chain density, ν_e , was calculated from Q by using Flory-Rehner's equation¹⁰. The value of interaction parameter between polymer and solvent is 0.38.

The measurement of the freezing point depression was carried out using an instrument designed by the authors, as described elsewhere².

RESULTS AND DISCUSSION

Figure 1(a) indicates the relationship between a_H and ν_e for nondegraded DCP-, TT- and sulphur-cured NR. a_H decreased with increasing ν_e . The decrease in a_H was not influenced by the different types of chemical structure at the crosslink sites. Further, the value of a_H could be extrapolated to zero at $Q=0$ within the experimental errors as shown in Figure 1(b). Since benzene does not exist as crystals in the gel at $Q=0$, the above relationship can be considered to be reasonable².

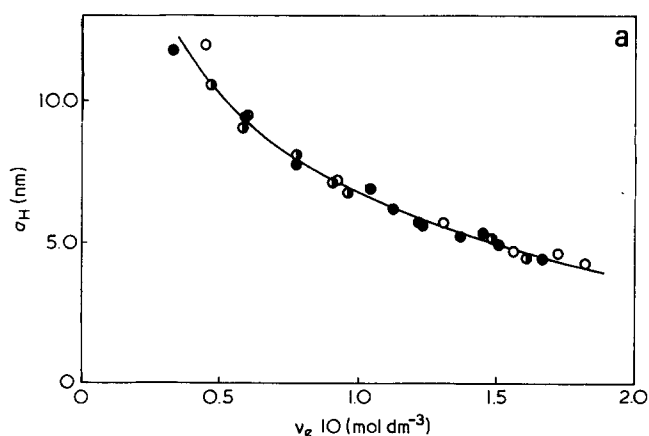


Figure 1 (a) Relationship between a_H and network chain density, ν_e , for ungraded rubber vulcanizates: ○, DCP-cured NR; ◐, TT-cured NR; ●, Sulphur-cured NR

Table 1 Preparations of natural rubber vulcanizates and the network chain densities for all samples

NR ^a	DCP ^b	TT ^c	St. Acid ^d	ZnO ^e	Sulphur	MBT ^f	Curing temperature (K)	Curing time (min)	10 ν_e (mol dm ⁻³) ^g
100	2						418	10	0.447
100	2						418	20	0.609
100	2						418	30	0.924
100	3						418	20	1.33
100	3						418	30	1.57
100	3						418	40	1.73
100	3						418	50	1.83
100		1	2	5			418	20	0.473
100		3	2	5			413	10	0.585
100		3	2	5			415	7	0.781
100		3	2	5			415	10	0.911
100		3	2	5			418	5	0.963
100		3	2	5			413	20	1.23
100		3	2	5			413	30	1.49
100		3	2	5			418	30	1.62
100			0.5	3	1	1	418	5	0.328
100			0.5	3	1	1	418	10	0.595
100			0.5	3	2	1	418	5	0.774
100			0.5	3	2	1	418	15	1.05
100			0.5	3	2	1	418	25	1.11
100			0.5	3	3	1	418	15	1.22
100			0.5	3	3	1	418	30	1.37
100			0.5	3	3	1	418	40	1.46
100			0.5	3	4.5	1	418	45	1.51
100			0.5	3	4.5	1	418	40	1.66

^a natural rubber; ^b dicumene peroxide; ^c tetramethylthiuramdisulphide; ^d stearic acid; ^e zinc oxide; ^f mercaptobenzothiazole; ^g samples were swollen in benzene at 303 K for 24 h

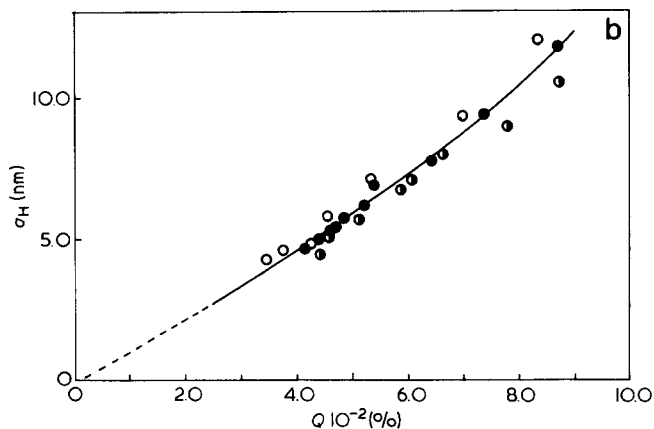


Figure 1 (b) Relationship between a_H and the degree of equilibrium swelling, Q , for undegraded rubber vulcanizates. Symbols as in Figure 1(a)

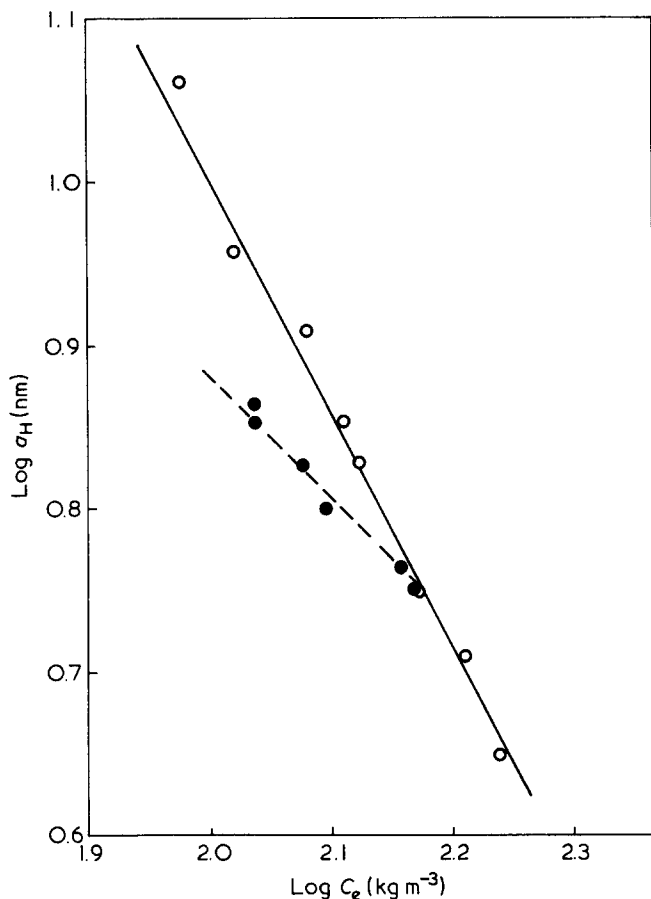


Figure 2 Dependence of $\log a_H$ on $\log C_e$. \circ , for an undegraded and \bullet , TT-cured NR degraded at 453 K in nitrogen. C_e is the swelling equilibrium concentration of polymer in the swollen rubber vulcanizates

Figure 2 shows the plots of $\log a_H$ versus $\log C_e$ for TT-cured NR degraded at 453 K in nitrogen and a non-degraded rubber vulcanizate. The scission of the network chains is generally said to occur near the crosslinkages under such conditions⁸. The value of m in equation (5) (obtained from the slope of the graph in Figure 2) was 1.13. This value of m is evidently different from the exponent in equation (2).

Figure 3 indicates the dependence of a_H on C_e for sulphur-cured NR degraded at 433 K in nitrogen and also for a nondegraded sample. The relationship between $\log a_H$ and $\log C_e$ for degraded samples, shown in Figure 3

was not linear. The variations in a_H are divided roughly into two stages in Figure 3. The division was carried out by reference to the chemical stress relaxation curve for sulphur-cured degraded NR (under the same conditions as shown in Figure 4). The relaxation curve could be

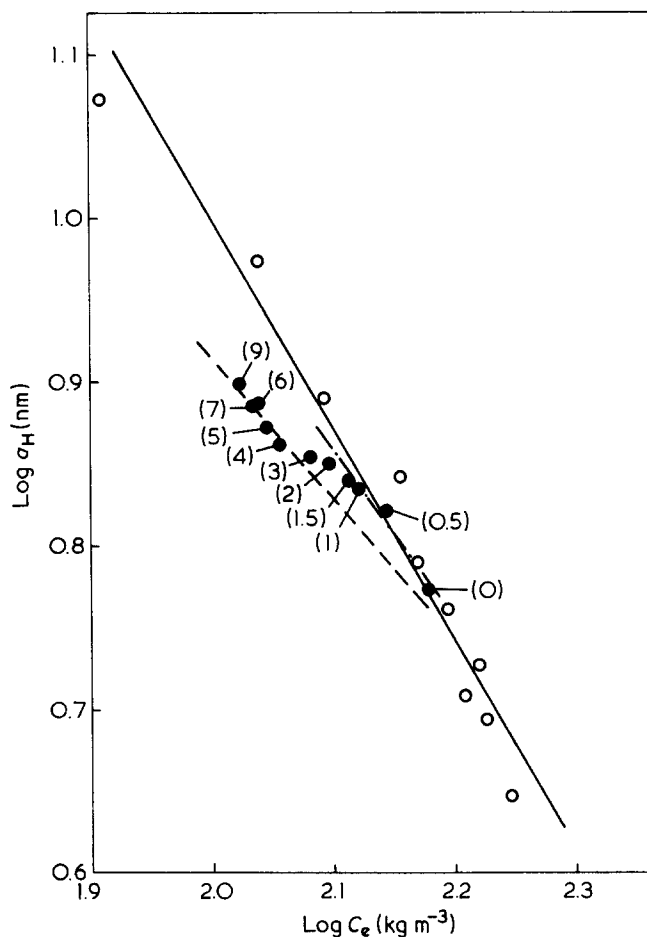


Figure 3 Plots of $\log a_H$ versus $\log C_e$ for, \circ , nondegraded sulphur-cured NR; and \bullet , degraded samples (samples degraded at 433 K in nitrogen). The values of m in equation (5) at the initial and the later stage of degradation were determined from the slope of the (---) line and of the (---) line, respectively. The figures in the brackets indicate the degradation time (h)

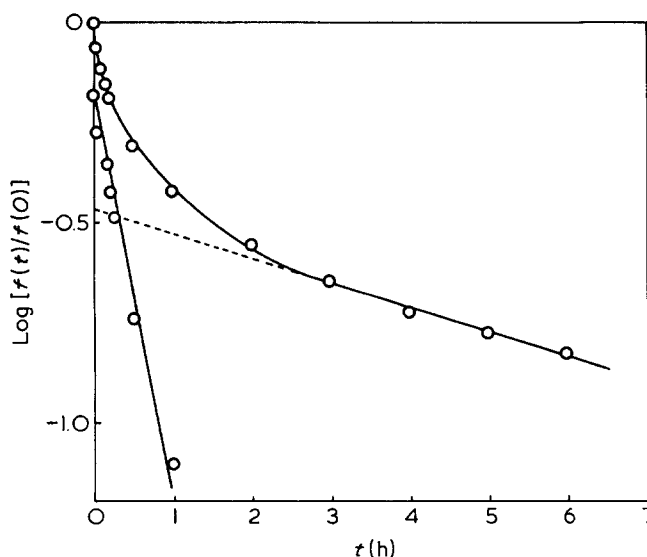


Figure 4 Continuous chemical stress relaxation curve for sulphur-cured NR degraded at 433 K in nitrogen. The relaxation curve can be expressed by the sum of two exponential terms by using 'Procedure X'⁷

expressed by the sum of two exponential terms⁷. In other words, the mechanism of degradation for sulphur-cured NR at the initial stage can be considered to be greatly different from that at the latter stage (i.e. after 3 h).

Then, $m = 1.15$ was calculated from the later changes of $\log a_H$ with $\log C_e$ (represented by ---- in Figure 3). This value agrees well with that obtained from the experimental results of thermal degradation for TT-cured NR in Figure 2. In the case of thermal degradation of sulphur-cured NR, it has been considered until now that the interchange reaction of polysulphide occurs at the initial stage of degradation, and that the scission of the network chains occurs mainly near the crosslinkages at the later stages. Thus, the mechanism of degradation at the later stage is said to be the same mechanism as thermal degradation for TT-cured NR⁸. The agreement between the value of m in Figure 2 and that at the later stage in Figure 3 suggests that the above interpretation may be reasonable. However, at the initial stage of degradation we obtained $m = 1.41$; a value which was obtained from the slope of the - - - - line in Figure 3.

The change of network structure based upon an interchange reaction of polysulphide for sulphur-cured NR will be further discussed in detail.

In the case of thermal degradation for sulphur-cured NR at 373 K in nitrogen, the relative value of the continuous stress relaxation, $f(t)/f(0)$, decayed to 20% lower at a degradation time $t = 10$ h than the initial value as shown in Figure 5. However, both of the relative network chain densities, $v_e(t)/v_e(0)$, and a_H were independent of degradation time and remained constant. From these experimental results only an interchange reaction can be considered to occur thermally under the above conditions. It follows that the network structure (especially the three-dimensional spatial network structure), is evidently not affected by the interchange reaction. In other words, fundamentally, the mechanism of the continuous stress relaxation caused by the interchange reaction can be considered to be valid⁷.

However, $v_e(t)/v_e(0)$ for sulphur-cured NR degraded at 393 K in nitrogen decreased to the extent of ~10% after 2-3 h, and afterwards the value of $v_e(t)/v_e(0)$ increased up to the initial value as shown in Figure 6. The variations of a_H were found to correspond to that of $v_e(t)/v_e(0)$. It is thought that the slight decrease of $v_e(t)/v_e(0)$ and increase

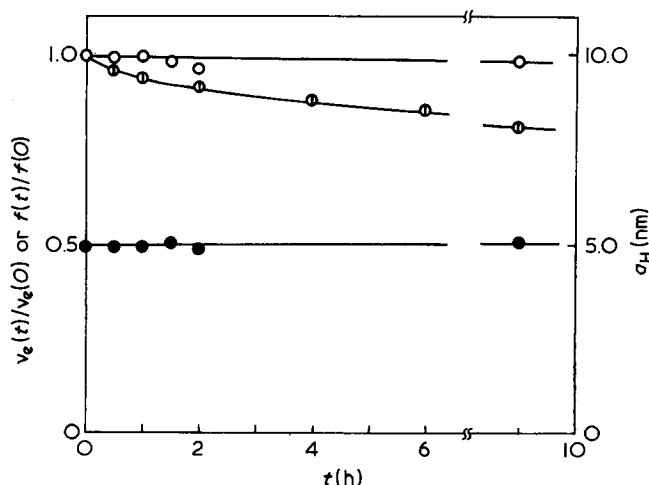


Figure 5 The variations of a_H , \bullet , the relative network chain densities, $v_e(t)/v_e(0)$, \circ , and the relative stress, $f(t)/f(0)$, \circ , for sulphur-cured NR degraded at 373 K in nitrogen

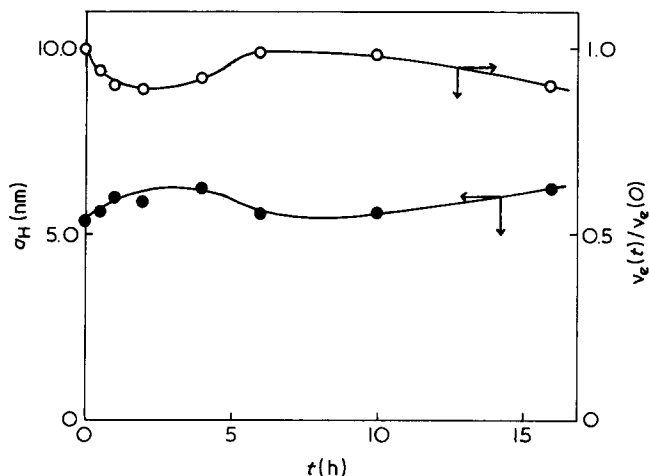


Figure 6 The variations of a_H and $v_e(t)/v_e(0)$ for sulphur-cured NR degraded at 393 K in nitrogen

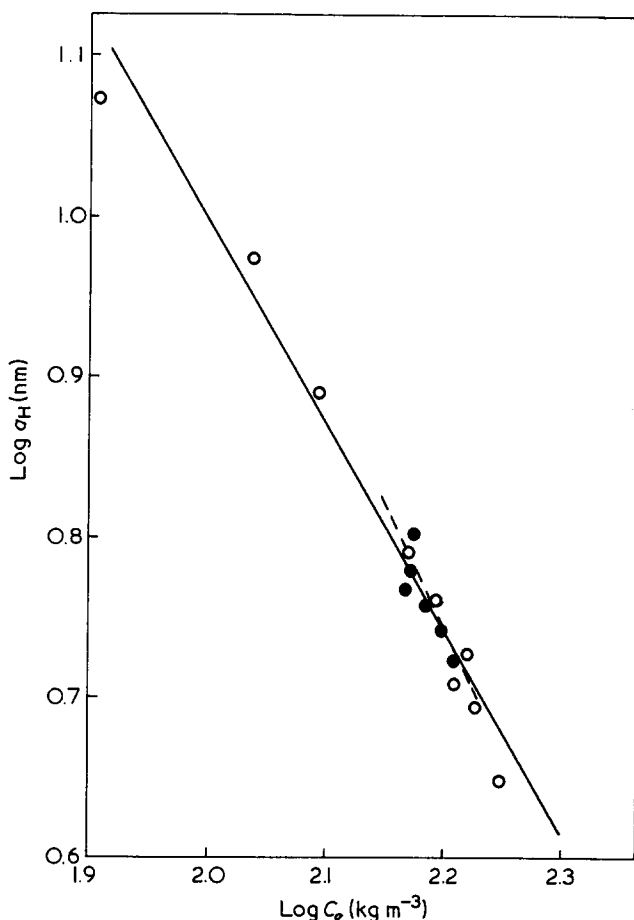


Table 7 The relationship between $\log a_H$ and $\log C_e$ for sulphur-cured NR: \circ , undegraded samples; \bullet , samples degraded at 393 K in nitrogen in the range of degradation time of 0-6 h

of a_H for thermally degraded samples for more than 10 h was due to degradation by the trace amounts of oxygen originally contained in the samples.

Figure 7 shows the plots of $\log a_H$ versus $\log C_e$ based on the same experimental results (with degradation times in the range of zero to six hours) as Figure 6. For a nondegraded sulphur-cured NR all the plots for samples degraded at 393 K in nitrogen are roughly linear. It follows that the three-dimensional spacial network structure degraded by the interchange reaction: may be phenomenologically similar to that for nondegraded

samples with various network chain densities. In this case the value of m was 2.08. At 393 K, in the presence of nitrogen the sole reaction to occur is the interchange reaction (see *Figures 6* and *7*). Because the soluble portion was undetectable in degraded rubber samples, it was possible to observe the decay of the continuous stress relaxation. The stress relaxation curve, however, did not perfectly correspond to the variations of $v_e(t)/v_e(0)$. In this way the variations of $v_e(t)/v_e(0)$ and a_H (see *Figures 6* and *7*) suggest that the dissociation of polysulphide at the crosslinking predominates over the formation of mono- and disulphides. On the contrary, both dissociation and formation may presumably be kept at equilibrium (in the case of thermal degradation at 373 K in nitrogen) as shown in *Figure 5*¹¹. Such a phenomenon would not be observed for degraded sulphur-cured NR with relatively high network chain densities of more than $\sim 1.40 \times 10^{-1}$ mol dm⁻³, even at 393 K. This is because the interchange reaction of polysulphide has already progressed for a long curing time¹².

It can therefore be assumed that the higher value of $m=1.41$ at the initial stage in *Figure 3* may reflect the change of the three-dimensional network structure. This is predominantly caused by the interchange reaction, as already shown in *Figures 6* and *7*.

In order to discuss in detail the dependence on the conditions of degradation shown by the exponent in equation (5), it is necessary to reveal the origin of the freezing point depression of the swelling solvent in swollen

rubber vulcanizates. This point must be clarified in future work.

CONCLUSION

It has become apparent that the exponent m in equation (5) reflects not only the difference in the three-dimensional network structure between degraded and a nondegraded rubber vulcanizates but it also reflects the differences under the various types of degradation (i.e. scission near the crosslink sites, interchange reactions of polysulphides at the crosslinkages and random scission along the main chains).

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