Studies of the network structure of rubber vulcanizates by a cryoscopic method: 3

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The freezing point depression of DCP-cured SBR with varying styrene content swollen in benzene was measured. The Kuhn parameter, a_H, decreased with increasing styrene content at the same swelling equilibrium concentration of polymer in swollen rubber vulcanizates, C_e. The dependence of a_H on styrene content and C_e could be explained qualitatively on the basis of the recent theory of semi-dilute polymer solutions. It was found from the difference in values of a_H that the three-dimensional structure of a degraded network at the initial stages of degradation may be different from that at the latter stages.

INTRODUCTION

The crosslink density or the network chain density is often the parameter used to characterize the network structure of crosslinked polymers such as rubber vulcanizates. It can be presumed from various experimental results that a real network structure is inhomogeneous where there is a molecular weight distribution of network chains between crosslinkages, with trapped entanglements occurring during the crosslinking process etc.[1]. However, reliable data relating to the inhomogeneous structure of a real network cannot be obatined solely from the above parameters, and it is difficult to evaluate such inhomogeneities within the real network structure. One can only estimate the changes in network structure, such as scission or crosslinking along main chains, mainly by chemorheological methods[1].

We have noticed that the freezing points of the diluents in swollen gels are remarkably depressed, and that the degree of depression, ΔT, is closely related to the crosslink density of the network as determined by the swelling method[2,3]. Furthermore, ΔT for a degraded sample was always larger than that for an undegraded sample, even if both types of samples have similar network chain densities. It therefore follows that ΔT reflects the difference in three-dimensional network structure between degraded and undegraded rubber vulcanizates[2,3].

In this article, styrene–butadiene rubber (SBR) vulcanizates were employed instead of vulcanized natural rubber, which was used in previous related studies. The dependence of ΔT on the styrene content of SBR will be discussed on the basis of the scaling concept, and the changes in network structure for thermo-oxidatively degraded SBR vulcanizates as revealed using a cryoscopic method.

EXPERIMENTAL

The materials used were styrene–butadiene rubber (SBR) of varying styrene content and *cis*-1,4-polybutadiene (PB), from the Japan Synthetic Rubber Co., Ltd. The

characteristics of the unvulcanized SBR and PB are summarized in *Table 1*. The content of styrene in SBR was determined from the refractive index of the solution of SBR in ethanol–toluene azeotrope[4]. The microstructure of the PB sequence in SBR[5] and the block index of SBR[6] were estimated using infra-red spectroscopy.

The rubber vulcanizate samples were prepared by milling DCP (dicumyl peroxide) with uncrosslinked SBR and PB followed by pressing at *ca.* 2 MPa at 418 K for given intervals. The crosslink density was controlled by the amounts of DCP and the curing time. All the samples were extracted with hot acetone for 24 h and dried *in vacuo*.

A degraded sample was immersed in benzene for 24 h at room temperature and dried *in vacuo*. The sample from which the soluble part of rubber (the sol) has already been 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 samples, and the network chain density, v_e, was calculated from Q by using the Flory–Rehner equation[7]. The interaction parameter values for the SBR (S4 sample) and/or the PB (S1 sample) and the solvent, χ, are 0.320 and 0.386, respectively.

The measurements of the freezing point depression[2] and chemical stress relaxation[1] were made using a conventional technique described elsewhere.

RESULTS AND DISCUSSION

Relationship between the magnitude of freezing point depression and styrene content in SBR vulcanizates

The quantitative description of the 'crystal size', a_H, of the swelling solvent in frozen swollen gels and its relation to the degree of freezing point depression, ΔT, was derived by Kuhn[8], who first paid some attention to such a phenomenon. If the swelling solvent is benzene and the structure factor of the crystal in Kuhn's equation is unity, the following relation can be obtained:

$$a_H = -35/\Delta T \text{ (nm)} \tag{1}$$

Table 1 Characterization of styrene–butadiene rubber (SBR)

| Sample | Styrene content[a] (mol%) | ρ (g cm^{-3}) | T_g (K) | Microstructure of polybutadiene sequence[b] | | | Block index[c] |
				cis-1,4 (%)	trans-1,4 (%)	vinyl-1,2 (%)	
S1[d]	0.0	0.914	195.2	97.1	1.8	1.1	–
S2	5.0	0.921	199.7	10.9	69.3	19.8	0.951
S3	12.0	0.930	206.5	10.9	70.3	18.8	0.931
S4	23.5	0.946	218.8	14.3	67.9	17.8	0.894
S5	46.0	0.977	248.3	30.9	53.7	15.5	0.997
S6	55.0	0.989	262.7	30.5	56.4	13.1	1.17
S7	65.0	1.00	280.9	37.8	50.2	12.0	1.20

[a] See ref. 4
[b] See ref. 5
[c] See ref. 6
[d] cis-1,4-polybutadiene

The crystal size was considered to be limited by the width of mesh size in the swollen networks.

However, since the value of a_H calculated from equation (1) is remarkably different from the crystal size determined by X-ray diffraction[9], a_H should be regarded as an 'indication', which varies inversely with ΔT, and may be associated with the three-dimensional spatial structure or mesh size of swollen networks or of gels[2,3].

Figure 1a shows the dependence of a_H, for DCP-cured SBR with various styrene contents and for DCP-cured PB, on v_e. It should be noted that as the crosslink density of the sample is lowered, a_H increases. Furthermore, a_H is decreased with increasing styrene content at the same values of v_e, and the degree of decrease, of a_H becomes marked at lower v_e values.

However, the values of a_H for all the samples could be extrapolated to zero at $Q = 0$, within the experimental error, as shown in *Figure 1b*. Since benzene does not exist as the crystal formed in the gels at $Q = 0$, the above relationship seems reasonable.

PB (sample S1) was regarded as the SBR with zero % styrene content. The broken line in *Figure 1a* indicates the relationship between a_H and v_e for sample S1, where the dependence of a_H on v_e and on styrene content differed from the other SBR samples. This unexpected result, as shown in *Figure 1a*, is considered to originate from the fact that v_e varies significantly with slight changes in χ in the Flory–Rehner equation. As described in the Experimental section, the χ value for sample S1 is different from that for sample S4. Moreover, as mentioned below, the increasing styrene content in SBR generally lowers the χ value.

However, experimentally to determine the crosslink density of samples using the Flory–Rehner equation does not apply here, since the χ values for all the samples have not been evaluated exactly. Therefore, the swelling equilibrium concentration of polymer in the swollen networks, C_e, is adopted instead of v_e. C_e is given by

$$C_e = \rho v_r \qquad (2)$$

where ρ and v_r are the density of sample and the volume fraction of rubber at the equilibrium swelling, respectively. Thus, C_e corresponds to the crosslink density.

Figure 2 shows the plots of $\log a_H$ vs. $\log C_e$ on the basis of the experimental results in *Figure 1a*. It is apparent that
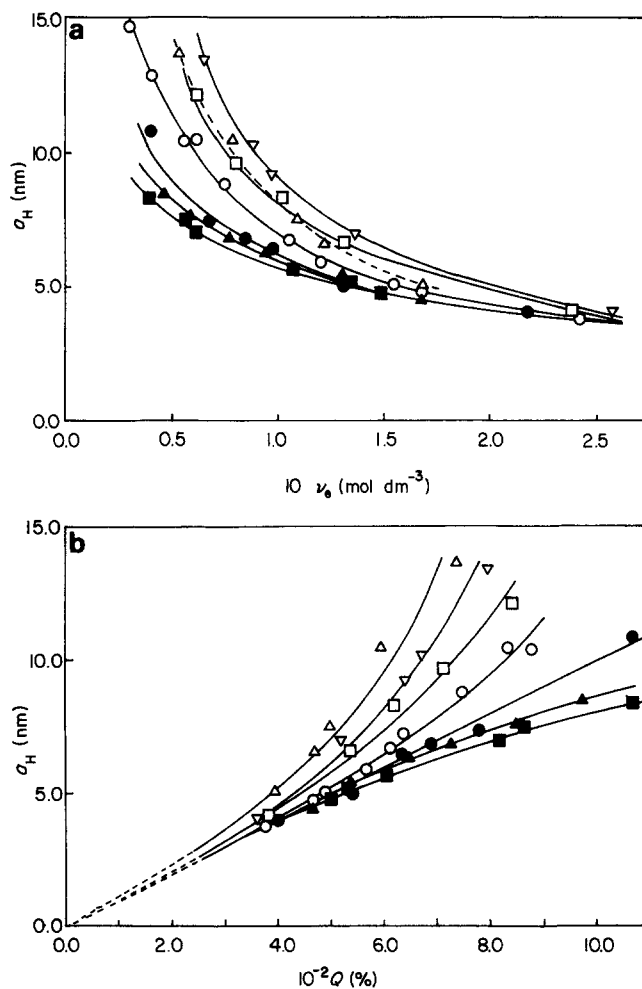

Figure 1 (a) Dependence of the crystal size, a_H, on the network chain density, v_e, for DCP-cured styrene–butadiene rubber (SBR) with various styrene contents: △, 0%; ▽, 5%; □, 12%; ○, 23.5%; ●, 46%; ▲, 55%; ■, 65%. (b) Depencence of a_H on the degree of equilibrium swelling, Q, for DCP-cured SBR with various styrene contents (same symbols)

an approximately linear relationship exists between $\log a_H$ and $\log C_e$. In other words, a_H decreases with increasing C_e and styrene content. The dependence of a_H on C_e can be experimentally represented by

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

where B is an experimentally determined constant. The

dependence of a_H on styrene content and C_e will be discussed below.

Figure 3 indicates the solubility parameter, δ, of SBR with varying styrene content and of other related materials[10]. The difference in the values of δ between SBR and benzene decreases with increasing styrene content. In other words, the compatibility between benzene and SBR with higher styrene contents improves, and the χ values diminish. It follows that a network of SBR vulcanizates with higher styrene content is increasingly more swollen and that the average mesh size becomes larger. The discussion given above is apparently in conflict with the experimental results shown in *Figure 2*. However, since the changes in χ values are attributable to the styrene content, the density of SBR vulcanizates, ρ, also varies. It is clear from equation (2) that the value of v_r changes with styrene content, even if C_e remains constant. Thus, the average molecular weight between crosslink sites, M_c, and/or the mesh size of the swollen networks vary with styrene content, even if C_e remains constant.

According to the analogy between semi-dilute polymer solutions and swollen networks on the basis of the scaling law (C^* theorem), the swelling of the elementary chains of the network, in a good solvent, is the same as that for equivalent chains at infinite dilution in the same solvent[11]. As a consequence, C_e can be identified with the cross-over concentration between the dilute and semi-dilute regions of a solution of polymer of the same molecular weight as the strands of the networks. Thus, C_e can be expressed by

$$C_e \propto M_c R_G^{-3} \tag{4}$$

Figure 3 Solubility parameter, δ, of SBR with various styrene contents, and δ for styrene, benzene, natural rubber and 1,3-butadiene

where R_G is the radius of gyration of network chains in the swollen state. In addition, R_G depends on M_c and χ as follows

$$R_G \propto (1-2\chi)^{1/5} M_c^{3/5} \tag{5}$$

Equation (5) suggests that the mesh size of the swollen network becomes larger, if the χ value decreases at the same M_c value. M_c being eliminated from equations (4) and (5), one can obtain

$$R_G \propto (1-2\chi)^{-1/4} C_e^{-3/4} \tag{6}$$

Figure 4 shows the theoretical curves calculated from equation (6). It is evident from *Figure 4* that R_G generally decreases with increasing C_e or with decreasing χ. Thus, R_G decreases at the same C_e, as the styrene content increases. The tendency of the theoretical curves in *Figure 4* is qualitatively compatible with the experimental results shown in *Figure 2*. Consequently, the dependence of a_H on the styrene content can be explained qualitatively by equation (6). However, the difference in microstructure of polybutadiene sequence in SBR does not greatly influence the relationship between a_H, χ and C_e.

Furthermore, it is suggested from the increase in the block index, as indicated in *Table 1*, that SBR may be transformed from a random copolymer into a block-like copolymer, and DCP-cured SBR is said to have a bundle-like crosslink structure in the PB part of SBR in which many chemical crosslink sites are concentrated[12]. As a result, the distribution of the mesh size in such a network structure of DCP-cured SBR is broadened with higher styrene content, and then the smaller mesh is formed in the networks. It follows that the value of a_H may then
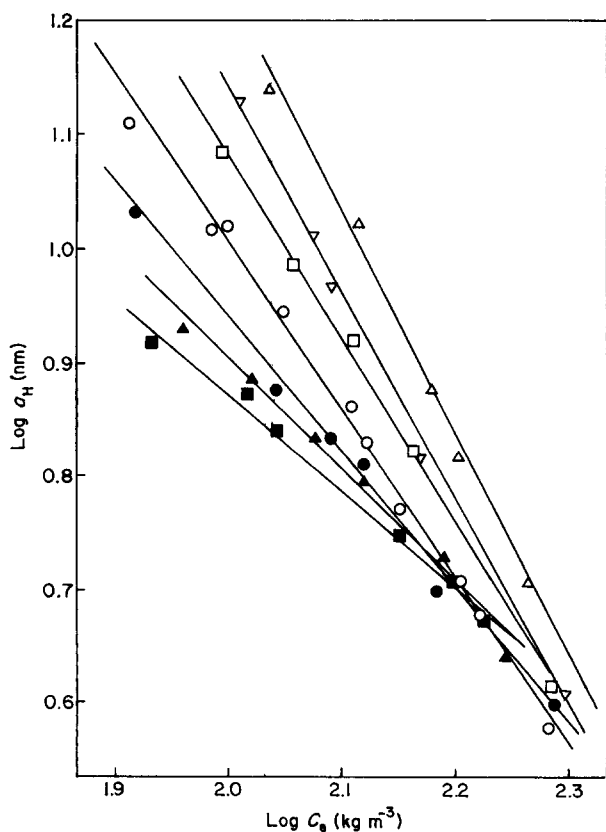
Figure 2 Relationship between $\log a_H$ and $\log C_e$ for DCP-cured SBR with various styrene contents. C_e is the swelling equilibrium concentration of polymer in the swollen rubber vulcanizates (symbols as in *Figure 1*)
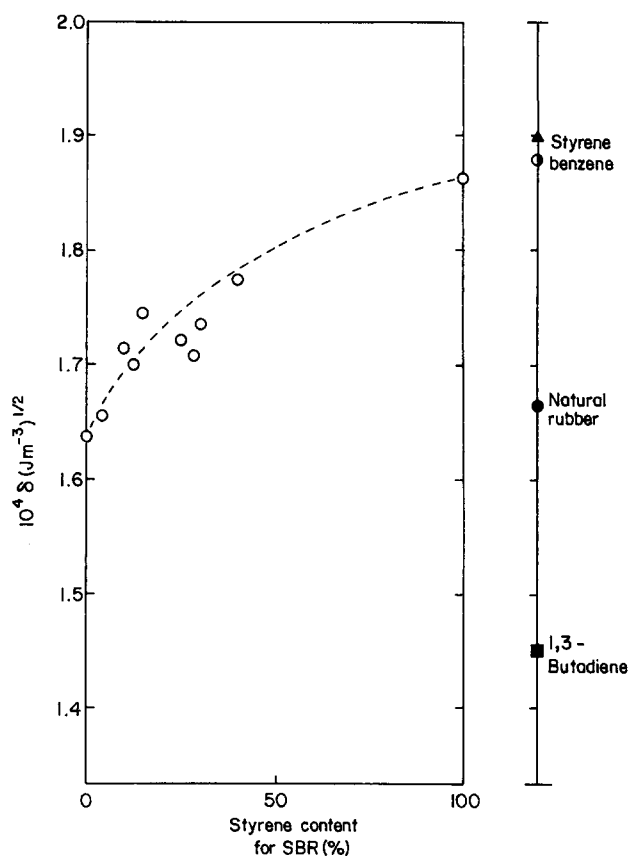
become lower. This is similar to the fact that a_H, for a degraded network in which the surviving smaller mesh still exists, becomes smaller than that for an undegraded network, even if both of them have apparently the same crosslink densities[2,3].

As already mentioned in previous studies[2,3], the screening length, ξ, of networks in a good solvent corresponds to the radius of gyration of network chains in
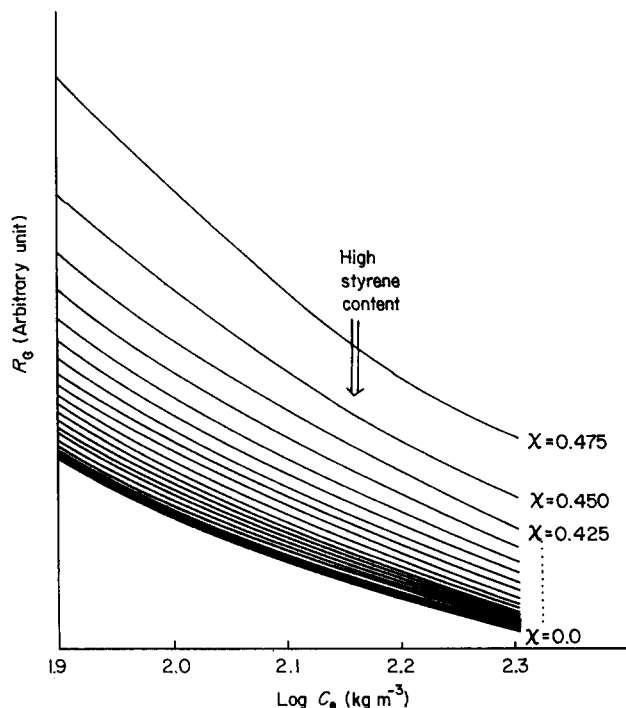

Figure 4 Theoretical curves based upon equation (6), which indicates the dependence of the radius of gyration of network chains between crosslinks, R_G, on the interaction parameter between polymer and solvent, χ, and C_e

swollen gels[11]:

$$\xi \simeq R_G \propto (1-2\chi)^{-1/4} C_e^{-3/4} \qquad (7)$$

Therefore, one can obtain the following equation from equations (3) and (7):

$$a_H \propto \xi^m \qquad (m=4B/3) \qquad (8)$$

where the exponent m is a constant determined by the experimental conditions. Aside from the definition of a_H by Kuhn[8], the physical meaning of a_H can be given experimentally by equation (8). The dependence of m on the styrene content is listed in *Table 2*.

Application of the cryoscopic method to degraded DCP-cured SBR in air

Figure 5 shows the chemical stress relaxation curves and the relative changes of v_e, $v_e(t)/v_e(0)$, for the DCP-cured sample S4 degraded at 383 K in air. Sample S4 is normally used as an industrial material. The remarkable increase in the intermittent stress relaxation, $f_i(t)/f_i(0)$, and of $v_e(t)/v_e(0)$ in the latter stage of degradation suggests that the crosslink reaction predominantly occurs in the degraded network. This fact is also supported by the decrease in the sol-fraction in degraded samples in the latter stage.

The variation in a_H for degraded DCP-cured sample S4 (under the above same conditions) is shown in *Figure 6*. As the scission reaction along main chains proceeds mainly at the initial stage of degradation, a_H increases with degradation time in the range of zero to *ca.* 4 h. Subsequently, a_H gradually decreases because of the crosslink reaction: a_H for the sample degraded for 15 h becomes *ca.* 60% less than the initial value.

Figure 7 shows the plots of log a_H vs. log C_e on the basis of the experimental results in *Figures 5* and *6*. The exponent m in equation (8) for a degraded sample was 1.06

Table 2 Dependence of exponent m on the experimental conditions

Rubber	Styrene content	Curing agent agent	Degradation conditions	m	Degradation mechanisms	Remarks
NR[a]		DCP[b]		2.00		
NR		TT[c]		2.01		
NR		Sulphur		2.01		
SBR[d]	0%	DCP		2.57		
SBR	5%	DCP		2.44		
SBR	12%	DCP		2.15		
SBR	23.5%	DCP		1.96		
SBR	46%	DCP		1.58		
SBR	55%	DCP		1.30		
SBR	65%	DCP		1.14		
NR		DCP	393 K in air	1.31		
NR		TT	393 K in air	1.33	Thermo-oxidative random scission	high crosslink density
				1.32		
NR		Sulphur	393 K in air	1.33	along main chain	
				(1.70)	Interchange reaction	low crosslink density
NR		TT	453 K in nitrogen	1.13	Chain scission near	
				1.15	the crosslinkages	
NR		Sulphur	433 K in nitrogen	1.41		
NR		Sulphur	373 K in nitrogen	–	Interchange reaction	
NR		Sulphur	393 K in nitrogen	2.04		
SBR	23.5%	DCP	383 K in air	1.06	Scission process	
				1.44	Crosslink process	

[a] natural rubber
[b] dicumene peroxide
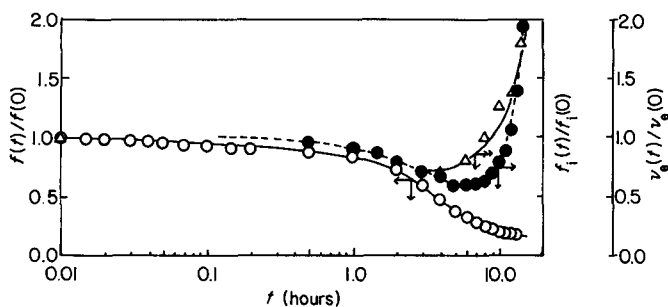[c] tetramethylthiuram disulphide
[d] styrene–butadiene rubber

Figure 5 Continuous, $f(t)/f(0)$, $\bigcirc$, and intermittent, $f_i(t)/f_i(0)$, $\bullet$, chemical stress relaxation curves, and the relative changes of network chain density, $v_e(t)/v_e(0)$, $\triangle$, for DCP-cured S4 sample degraded at 383 K in air
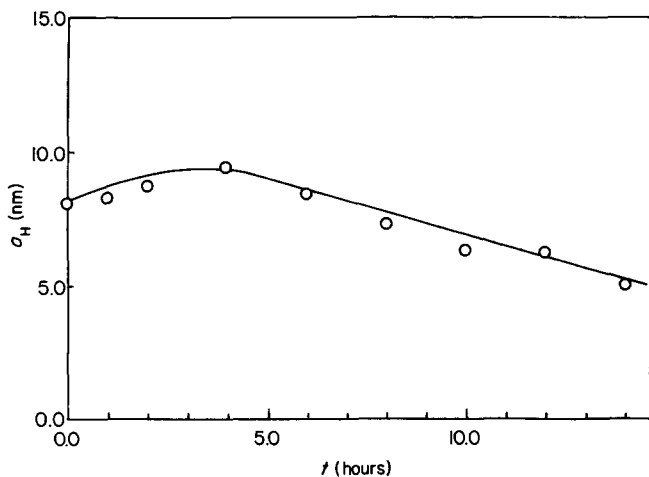

Figure 6 Variation of a_H for DCP-cured sample S4 degraded at 383 K in air

Figure 7 Plots of log a_H vs. log C_e for DCP-cured samples S4: $\bigcirc$, undegraded samples; $\bullet$, samples degraded at 383 K in air at the initial stage (range of degradation time = 0–4 h); $\blacktriangle$, samples degraded under the same conditions at the later stage (range of degradation time of more than 4 h)

at the initial stage, whereas it was 1.44 at the later stage of degradation.

R_G or the mesh size in the swollen state is essentially determined by equation (6). In other words, R_G for an undegraded network must be the same as that for a degraded one, if both types of samples have the same crosslink densities. However, a degraded network structure is considered to be different from an undegraded one, even if the crosslink densities or C_e values are in agreement[3]. To the contrary, however, a_H can reflect the difference in the network structure, as shown in *Figure 7*, and the exponent m indicates experimentally the extent of such a difference. Thus, it has become apparent from such differences in the values of m that the three-dimensional structure of the network at the initial stage of degradation is different from that at the latter stage, even if, at both stages, the crosslink densities or C_e values are apparently the same. Moreover, the degraded network structure of the DCP-cured SBR was clearly distinct from the undegraded structure.

It is well known that the crosslink reaction based upon thermo-oxidation occurs mainly near the surface of SBR vulcanizates[1,13,14]. It then follows that the network structure near the surface, at the latter stage of degradation, is expected to be more dense than the interior structure, and therefore the mesh size near the surface may be smaller than that for the interior. Consequently, the distribution of mesh size in the degraded network is considered to be broadened in the latter stage of degradation. The above discussion can explain qualitatively the experimental results shown in *Figure 7*.
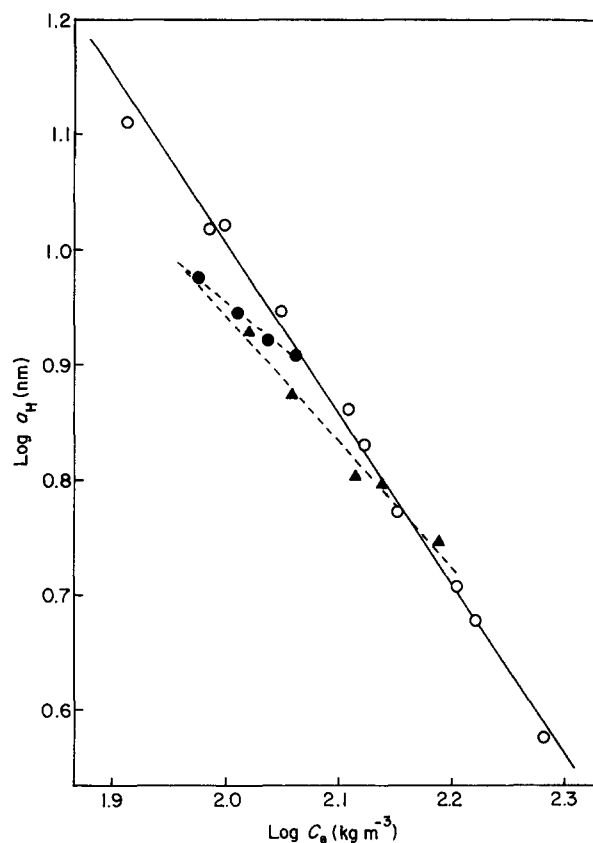
Finally, the dependence of the exponent m on the types of vulcanization, the ratio of composition of copolymers and the conditions of degradation are summarized in *Table 2* along with the mechanism of degradation. A part of the data in *Table 2* has been reported previously[2,3].

CONCLUSION

It has become apparent that a_H or the exponent m in equation (8) can reflect not only the difference in mesh size of the swollen network of DCP-cured SBR with various styrene contents, but also the changes in network structure of SBR vulcanizates degraded in air, in spite of the samples having the same crosslink densities.

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