

# Studies of network structure of rubber vulcanizates by a cryoscopic method: 4

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(Received 30 September 1985; revised 3 December 1985)

The freezing-point depression (FPD),  $\Delta T$ , for unimodal and bimodal end-linked poly(dimethyl siloxane) (PDMS) networks swollen in benzene was measured. The crystal size parameter of benzene in frozen swollen networks,  $a_H$ , introduced by Kuhn, which varies inversely as  $\Delta T$ , was experimentally confirmed to be associated with the screening length and/or the radius of gyration of the network chain in swollen gels by using an expression of power-law type, and to reflect the inhomogeneity of network structure. Further, the values of  $a_H$  of bimodal PDMS networks became lower than those of unimodal ones at the same equilibrium concentration of polymer in the swollen networks. Such a tendency was phenomenologically similar to that observed for degraded networks of rubber vulcanizates as compared with undegraded ones. Some discussion with respect to this fact has been carried out on the basis of the origin of FPD.

(Keywords: poly(dimethyl siloxane); end-linked model network; freezing point depression; screening length; stress relaxation)

## INTRODUCTION

Network structure of swollen rubber vulcanizates has been studied by a cryoscopic method<sup>1-3</sup>. A crosslinked rubber polymer swollen in a diluent such as benzene is cooled, and then a large freezing point depression (FPD) of the swelling solvent is observed. The degree of FPD,  $\Delta T$ , increased with the crosslink density of samples and was not affected by the types of chemical structure at the crosslink sites in the case of natural rubber vulcanizates<sup>2</sup>. On the other hand, the freezing point for vulcanized styrene-butadiene rubber (SBR) swollen in benzene was largely depressed with increasing styrene content, in spite of the same crosslink densities<sup>3</sup>. The compatibility between SBR and benzene becomes better with higher styrene content, and then the interaction parameter between polymer and solvent,  $\chi$ , diminishes. In other words, the smaller the  $\chi$  value is, the larger  $\Delta T$  becomes. Moreover,  $\Delta T$  for degraded rubber vulcanizates became generally larger than that for undegraded ones, if both of them have apparently the same crosslink densities<sup>1-3</sup>.

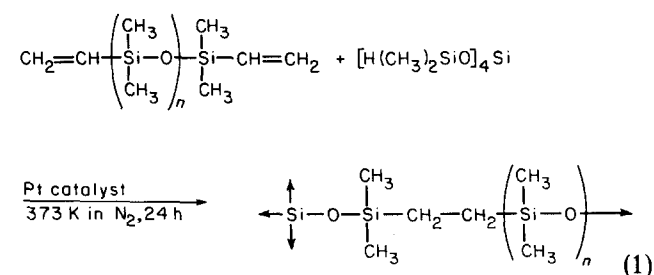
Kuhn first paid attention to this phenomenon. According to Kuhn's assumption, the 'size of crystal' grown in frozen swollen gels was limited in size by the 'mesh' width of swollen networks, and the crystal size was defined as the parameter,  $a_H$ , which varies inversely as  $\Delta T$ .<sup>4</sup> The experimental result mentioned above implies that  $a_H$  can reflect not only the mesh size of swollen network in rubber vulcanizates, which corresponds to the crosslink density, but also the difference in three-dimensional structure between undegraded and degraded networks<sup>1-3</sup>. On the other hand, the value of  $a_H$  was remarkably different from the crystal size determined by using X-ray diffraction<sup>5</sup>. So, the authors have proposed that  $a_H$  should be regarded as a 'measure', which may be closely associated with the three-dimensional structure of swollen networks or gels<sup>1</sup>. Thus  $a_H$  could be experimentally correlated to the screening length by

means of an expression of power-law type on the basis of the so-called C\* theorem, which points out the analogy between semi-dilute polymer solution and swollen gel<sup>6</sup>. The screening length corresponds to the radius of gyration of network chains in swollen gel. The exponent in the power law was greatly dependent upon the conditions of degradation and upon the compositions of copolymers<sup>3</sup>.

In this article, the proposed physical meaning of the parameter  $a_H$  will be experimentally confirmed by using end-linked poly(dimethyl siloxane) (PDMS) model networks. Further, the difference in values of  $a_H$  between an undegraded network and a degraded one will be discussed with reference to the comparison of  $a_H$  of unimodal PDMS network with that of bimodal one.

## EXPERIMENTAL

Prepolymers used in the present study were four kinds of  $\alpha,\omega$ -divinyl poly(dimethyl siloxane) (PDMS). Tetra(dimethylhydrosiloxy)silane was employed as the crosslink agent. The crosslink sites in PDMS networks are tetrafunctional, and formed by the highly selective addition of Si-H groups in the crosslink agent to vinyl groups on prepolymers<sup>7</sup>:



This reaction goes essentially to completion with no side reaction, isomerization or by-products<sup>8</sup>. The con-

centration of vinyl groups on prepolymers was determined by Wij's test<sup>9</sup>, and then the number-average molecular weight of prepolymers,  $M_n$ , the content of vinyl groups and the number of vinyl groups per chain could be calculated.  $M_n$  estimated from Wij's test was in fair agreement with that determined by gel permeation chromatography (g.p.c.) in toluene. The index of inhomogeneity became less than 2 from the measurements of g.p.c. in any prepolymer. All the prepolymers were characterized to have vinyl groups at both ends of at least 95% of the chains from the number of vinyl groups per chain. Unreacted vinyl groups in crosslinked PDMS samples were determined by Wij's test in the same manner<sup>9</sup>. The extent of reaction was calculated from the variations of concentration of vinyl groups in the reactants. All the parameters already described are summarized in Table 1.

The detailed experimental procedures will be mentioned below<sup>7</sup>. First, the prepolymer, the crosslink agent and Pt catalyst ( $H_2[PtCl_6] \cdot 6H_2O$ , 5 wt% 2-propanol solution) were violently mixed in the absence of diluent. The silane crosslink agent was present to an extent corresponding to 1:1 molar ratio between active hydrogen atoms and vinyl groups, thus giving crosslinks of average functionality 4.<sup>8</sup> However, the molar ratio was 1.5:1 in the case of sample D. Pt catalyst also exists in an amount corresponding to 5–10 ppm of elemental Pt relative to the total weight of the reactants. The mixture was poured into a Teflon mould, degassed, and cured at 373 K in nitrogen for 24 h. The resulting crosslinked polymers were extracted in benzene for four days at room temperature, deswelled carefully in benzene/methanol mixture, and dried *in vacuo*. The sol fraction was less than 5 wt% in any sample.

Besides unimodal PDMS model networks mentioned above, bimodal ones were prepared as shown in Table 2<sup>10</sup>. There were four kinds of prepolymers, which were mixtures of samples A and D having compositions listed

**Table 1** Characterizations of linear poly(dimethyl siloxane) (PDMS) prepolymers and preparations of end-linked unimodal PDMS model networks

Sample	$M_n$ (g mol <sup>-1</sup> )		Vinyl content (%)	Number of vinyl groups per chain	Extent of reaction (%)
	G.p.c.	Wij's test			
A	$2.36 \times 10^3$	$2.64 \times 10^3$	89.4	1.8	90.2
B	$9.36 \times 10^3$	$9.76 \times 10^3$	95.8	1.9	92.7
C	$1.59 \times 10^4$	$1.13 \times 10^4$	99.9	2.0	70.1
D	$4.19 \times 10^4$	$4.08 \times 10^4$	99.9	2.0	79.2

$[H(CH_3)_2SiO]_4Si$ :  $\rho = 8.87 \times 10^2$  kg m<sup>-3</sup>  
 Linear PDMS chain:  $\rho = 9.70 \times 10^2$  kg m<sup>-3</sup>  
 [Linear PDMS]:[crosslink agent] = 2:1 (3:1 for sample D)  
 Pt catalyst: 5–10 ppm elemental Pt relative to the total weight of reactants

**Table 2** Preparations and characterizations of end-linked bimodal PDMS model networks

Sample	Content of sample A		$M_n$ , calc. (g mol <sup>-1</sup> )	Extent of reaction (%)
	Wt%	Mol%		
AD-2	80	98.3	$3.71 \times 10^3$	88.0
AD-4	60	95.7	$5.08 \times 10^3$	87.6
AD-6	40	90.8	$7.64 \times 10^3$	79.3
AD-8	20	78.9	$1.39 \times 10^4$	72.0

in columns 2 and 3 of Table 2.  $M_n$  of the mixed prepolymer was calculated from the ratio of mixture and  $M_n$  values of samples A and D. The other parts of experiments have been carried out in the same manner.

The equilibrium degree of swelling,  $Q$  (%), was determined from the increment of the weight of swollen crosslinked PDMS samples in benzene, and the network chain density,  $v_c$ , was calculated from  $Q$  by using the Flory–Rehner equation<sup>11</sup>. The value of interaction parameter between PDMS and solvent,  $\chi$ , is given by<sup>12</sup>

$$\chi = 0.484 + 0.33v_r \quad (\text{benzene, 303 K}) \quad (2)$$

where  $v_r$  is the volume fraction of rubber, equal to  $100/(100+Q)$ .

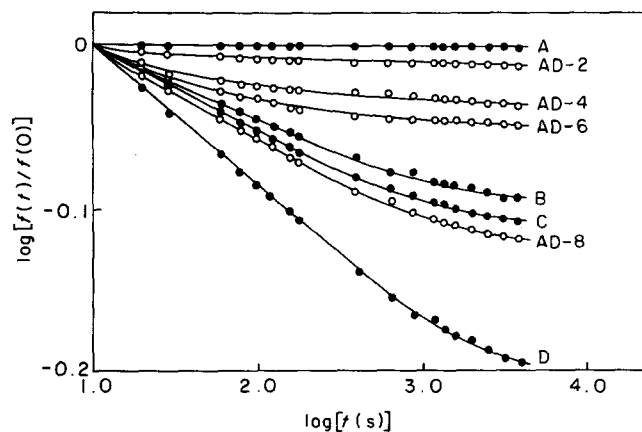
The measurements of FPD<sup>1</sup> and the uniaxial compressive stress relaxation<sup>13</sup> were carried out with the conventional method (JSR, Stress Relaxation Instrument, No. 1) as described elsewhere.

## RESULTS AND DISCUSSION

Figure 1 shows the uniaxial compressive stress relaxation curves for unimodal and bimodal crosslinked PDMS samples. Stress reached almost the equilibrium value in about 1 h except for sample D. The logarithm of relative stress,  $f(t)/f(0)$ , decreased linearly against the logarithm of time at the initial stage (for approximately 5 min after compression)<sup>14</sup>. On the other hand, plots of  $\log[f(t)/f(0)]$  vs.  $\log t$  for bimodal samples did not exhibit such a good linear relation as those of unimodal ones during the same period. The difference in these behaviours is considered to be attributable to the distinction between a unimodal network and a bimodal one mentioned later. Here, the value of stress at 1 h was regarded as the equilibrium value. The relative magnitude of the equilibrium stress decreased as  $M_n$  of prepolymers became larger. According to the statistical theory of rubber-like elasticity, the relationship between stress,  $f$ , and the average molecular weight between crosslinkages,  $M_c$ , in rubber vulcanizates is expressed by<sup>15</sup>

$$f^* \equiv f/(\alpha - \alpha^{-2}) = (\rho/M_c)RT \quad (3)$$

where  $f^*$  denotes the reduced force,  $\alpha$  is compression (or extension) ratio, and  $\rho$ ,  $R$  and  $T$  are the density of sample, gas constant and absolute temperature, respectively.



**Figure 1** Uniaxial compressive stress relaxation curves for end-linked unimodal and bimodal poly(dimethyl siloxane) (PDMS) networks at 308 K in nitrogen. Compression ratio,  $\alpha$ , is  $\sim 0.9$

From the demand of the theory, the equilibrium stress must be measured at small deformation in order to use equation (3).

Figure 2 indicates the dependence of  $f^*$  determined from the equilibrium stress as defined in Figure 1 on the reciprocal of  $M_c$ ,  $M_c^{-1}$ , calculated by equation (3). The relationship between  $f^*$  and the inverse of  $M_n$ ,  $M_n^{-1}$ , for each prepolymer is also represented in Figure 2.

For the end-linked PDMS model network used in the present study, if all the prepolymers have functional groups at both ends of the chain and the curing has completely proceeded,  $M_c$  is expected to be equal to  $M_n$ .<sup>16</sup> Also, if one considers the effect of entanglements along network chains,  $M_c$  determined by using mechanical techniques such as stress-strain measurement must become less than  $M_n$ .<sup>16</sup> In Figure 2, however,  $M_c$  is approximately twice as large as  $M_n$  in any crosslinked PDMS. Two main reasons can be considered to account for such experimental results: one is that the extent of reaction is less than 100% as shown in Tables 1 and 2; the other is an assumption of affine deformation in deriving equation (3). Since the extent of reaction is less than 100%, some dangling chains exist in real PDMS model networks, and these dangling chains are mechanically ineffective. It follows that the crosslink density determined by using a mechanical method becomes lower, and that  $M_c$  becomes larger than  $M_n$ . Further, the behaviour of real rubber vulcanizates is said to become intermediate between affine and phantom deformation from many experiments based upon the recently advanced theory of rubber elasticity<sup>16,17</sup>.  $M_c$

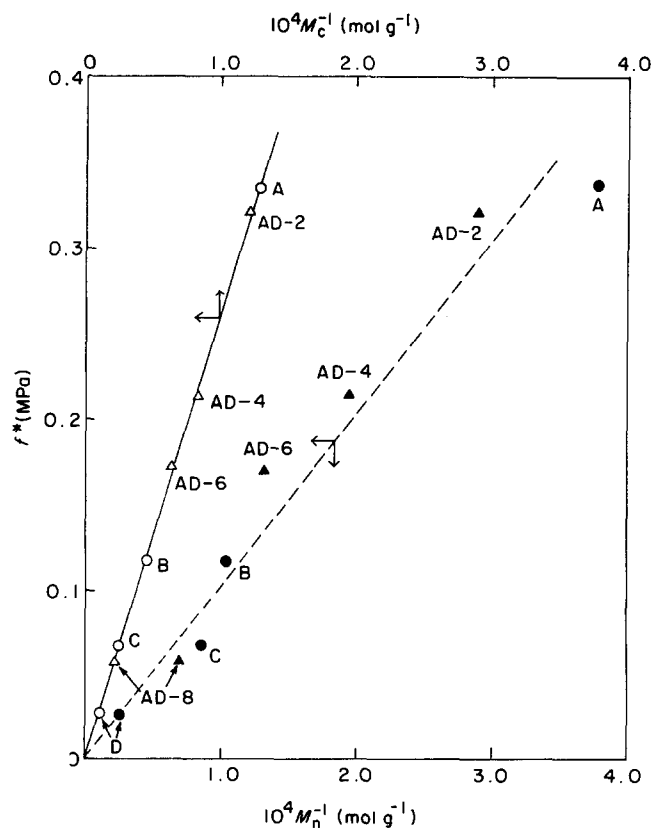


Figure 2 The relationship between the reduced force,  $f^*$ , and the reciprocal of  $M_c$  and  $M_n$  for various PDMS networks.  $M_c$  calculated by equation (3) denotes the average molecular weight between crosslinks, and  $M_n$  is the number-average molecular weight of PDMS prepolymers listed in Tables 1 and 2

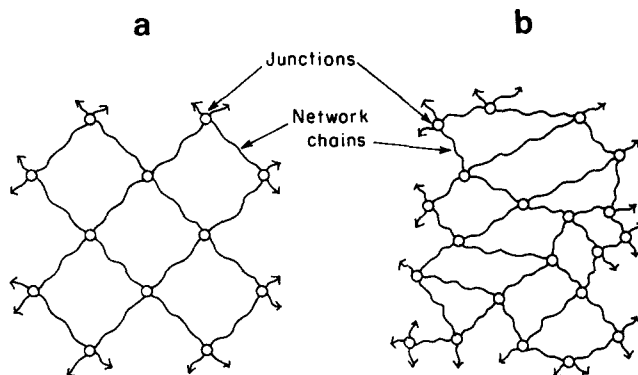


Figure 3 Scheme of end-linked PDMS model networks: (a) unimodal network; (b) bimodal one. The arrows indicate that the network chains are connected with surrounding infinite gels

becomes overestimated, since equation (3) was derived on the assumption of affine deformation.

In Figure 2, it is of importance and interest that the dependence of  $f^*$  on  $M_n^{-1}$  is approximately linear, though the relation shows some scatter. In other words, the relations between  $f^*$  and  $M_n^{-1}$  for unimodal PDMS networks are clearly indistinguishable from those for bimodal ones. This fact will be discussed in detail below.

Schemes of unimodal and bimodal PDMS model networks are shown in Figure 3. The molecular weights between crosslinks are almost equal to each other in a unimodal network, and hence the mesh size may be homogeneous. On the other hand, a distribution in molecular weight between crosslink sites is present in a bimodal network: a distribution in mesh size exists, and hence the network can be regarded as more inhomogeneous. Recently, the theory of rubber-like elasticity has been advanced<sup>17</sup>. However, since the theoretical result is fundamentally derived from the statistical treatment of the changes of elastic free energy with deformation, the parameter which represents the effect of the distribution in molecular weight of network chains is not involved in the derived result. Only an 'average' molecular weight of network chain is estimated from an expression similar to equation (3). Thus, basic information with respect to the inhomogeneity of network structure, i.e. the distribution in mesh size, as shown in Figure 3, cannot be obtained from a mechanical technique such as stress-strain measurement.

In contrast, as mentioned below, the difference in network structure between unimodal and bimodal PDMS networks could be revealed by using a cryoscopic method.

Figure 4 indicates that the freezing point,  $T_m$ , of benzene in swollen unimodal crosslinked PDMS samples is depressed with increasing volume fraction of rubber,  $v_r$ . The magnitude of FPD is much larger than that of PDMS prepolymer (sample D) solution in benzene. Such a tendency is similar to that of the natural rubber (NR)/benzene system<sup>1</sup>, and hence  $T_m$  of swollen gels is remarkably lower than that of polymer solutions at the same  $v_r$ .

The parameter of 'crystal size',  $a_H$ , which was introduced by Kuhn, is expressed by the following equation, if the swelling solvent is benzene and the structural factor of the crystal in Kuhn's original equation is unity<sup>4</sup>:

$$a_H = -35/\Delta T \quad (\text{nm}) \quad (4)$$

where  $\Delta T$  is the degree of FPD.

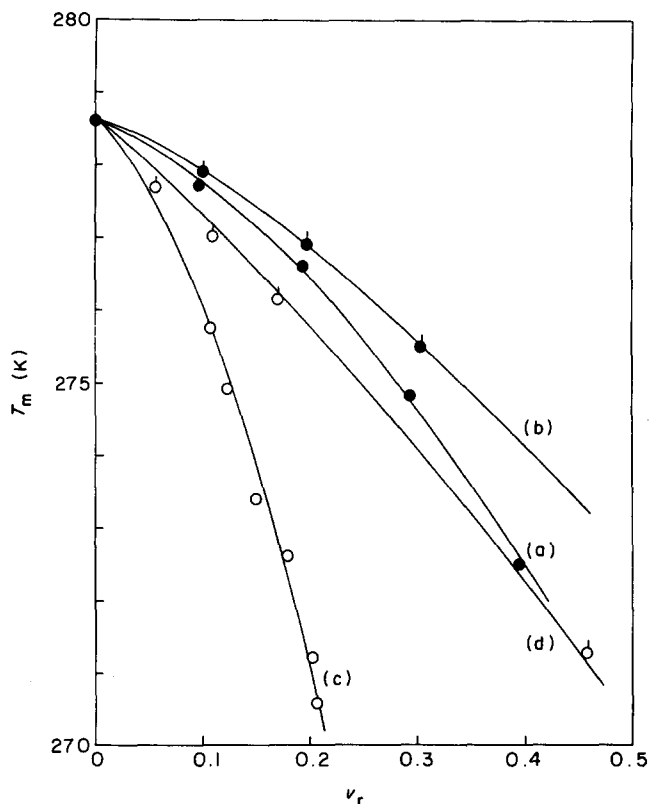


Figure 4 The dependence of the freezing point of benzene,  $T_m$ , on the volume fraction of rubber,  $v_r$ : (a) natural rubber (NR) and (b) PDMS solutions in benzene; (c) dicumene peroxide (DCP) cured NR and (d) unimodal PDMS networks swollen in benzene

The relationship between  $a_H$ ,  $v_e$  and  $Q$  for unimodal PDMS networks is shown in Figure 5a, and the same relation for bimodal networks in Figure 5b. In both cases,  $a_H$  decreased with increasing  $v_e$ , and the values of  $a_H$  could be extrapolated to zero at  $Q=0$  within the experimental errors in Figures 5a and b. Since benzene does not exist as crystal in the gel at  $Q=0$ , the above relationship is reasonable. It should be noted in Figures 5a and b that the values of  $a_H$  for unimodal PDMS networks are different from and higher than those for bimodal ones, even if both types of samples have apparently the same crosslink densities.

By the way, the absolute values of  $v_e$  for the samples with lower crosslink densities became significantly smaller than those estimated from  $M_n$  of PDMS prepolymers ( $v_e = \rho/M_n$ ) by calculation in Figure 5 because benzene is a moderately good solvent for PDMS and  $\chi$  parameter is close to 0.5 (equation 2). Further, there are some problems on the derivation of the conventional Flory-Rehner equation<sup>16</sup>, and its modification is now being attempted on the basis of the recently advanced theory of rubber-like elasticity<sup>17</sup>.

So, since it is not appropriate to determine experimentally the crosslink density of samples by using the Flory-Rehner equation, the swelling equilibrium concentration of polymer in swollen networks,  $C_e$ , was adopted as a measure of crosslink density instead of  $v_e$ .  $C_e$  is defined as

$$C_e = \rho v_r \quad (5)$$

Figure 6 indicates the plots of  $\log a_H$  vs.  $\log C_e$  based upon the experimental results in Figures 5a and b. Good

linear relations between  $\log a_H$  and  $\log C_e$  were obtained for both unimodal and bimodal PDMS networks. According to the recent theory of semi-dilute polymer solutions,  $C_e$  can be identified with the so-called cross-over concentration between the dilute and semi-dilute regions of solution of polymers of the same molecular weight as the strands of the networks ( $C^*$  theorem)<sup>6</sup>. So, the screening length,  $\xi$ , which corresponds to the radius of gyration of network chains in swollen gel, is expressed by<sup>1,6</sup>

$$\xi \sim C_e^{-3/4} \quad (6)$$

The dependence of  $a_H$  on  $C_e$  could be experimentally represented by

$$a_H \sim C_e^{-B} \quad (B > 0) \quad (7)$$

where  $B$  is a constant determined experimentally. Therefore, one can obtain

$$a_H \sim \xi^m \quad (m = 4B/3) \quad (8)$$

The parameter of  $a_H$  which was regarded as a measure of the three-dimensional structure or of the mesh size of swollen networks can be experimentally given a

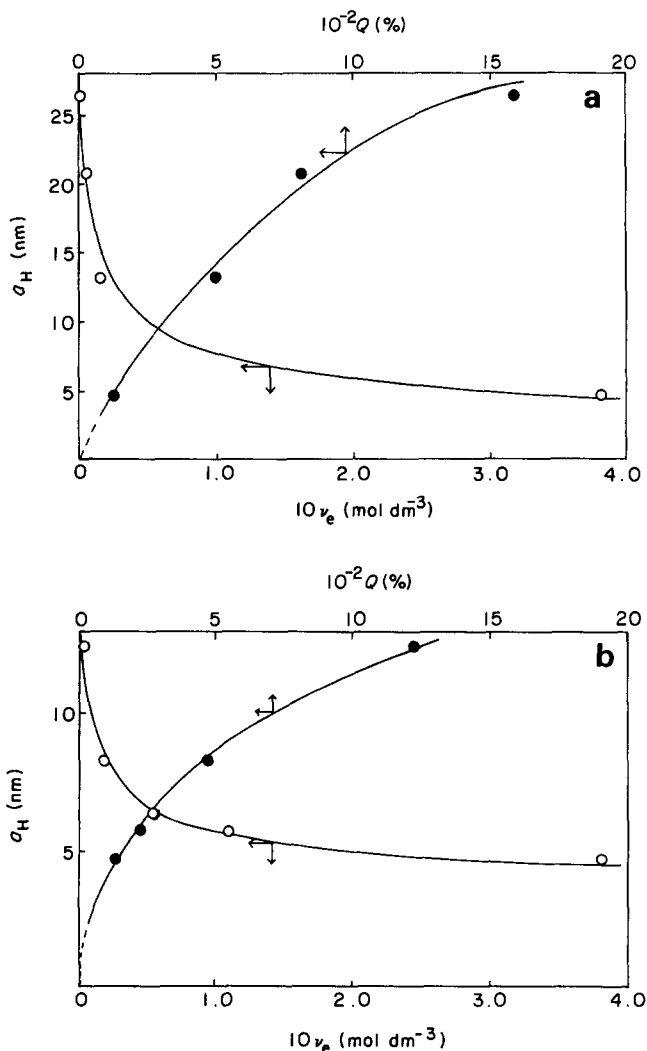
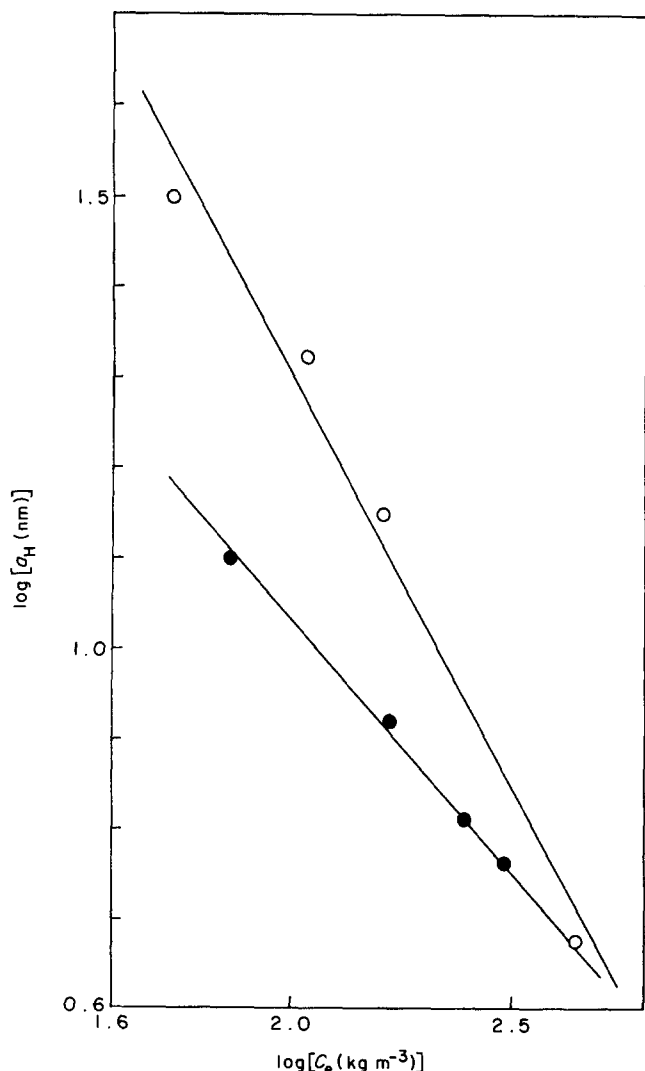


Figure 5 (a) The relationship between the crystal size (Kuhn's parameter)  $a_H$ , the degree of equilibrium swelling  $Q$ , and the network chain density  $v_e$ , for unimodal PDMS networks. (b) The relationship between  $a_H$ ,  $Q$  and  $v_e$  for bimodal PDMS networks



**Figure 6** Plots of  $\log a_H$  vs.  $\log C_e$  for unimodal (○) and bimodal (●) PDMS networks.  $C_e$  is the swelling equilibrium concentration of polymer in the swollen rubber vulcanizates

physical meaning by the relation (8). In *Figure 6*

$$a_H \sim \zeta^{1.16} \quad \text{for unimodal network} \quad (9)$$

$$a_H \sim \zeta^{0.76} \quad \text{for bimodal network} \quad (10)$$

Now, the radius of gyration of network chain,  $R_G$ , in swollen gel at the equilibrium swelling can be estimated on the basis of the  $C^*$  theorem, since the average molecular weight of network chain,  $M_c$ , is known in the case of an end-linked model network. It is assumed that  $M_c$  of each crosslinked PDMS is equal to  $M_n$  of prepolymers listed in *Tables 1* and *2* because of the nature and near-completeness of the end-linked reaction<sup>16</sup>.  $R_G$  for a network swollen in a good solvent is generally expressed by<sup>6</sup>

$$R_G \sim aM_c^v \sim aM_n^v \quad (11)$$

where  $a$  and  $v$  are a monomer length and the universal exponent, respectively. The value of  $v$  is close to 0.6 for a good solvent<sup>6</sup>. The value of  $a$  was taken as 0.378 nm, which was estimated from a small-angle neutron scattering experiment<sup>18</sup>. However, since the numerical

coefficient in equation (11) is unknown, the calculated  $R_G$  itself becomes an arbitrary value.

*Figure 7* shows the dependence of  $\log R_G$  on  $\log C_e$  for unimodal and bimodal networks. The straight line in *Figure 7* was drawn by the least-squares method. One can obtain the following relation:

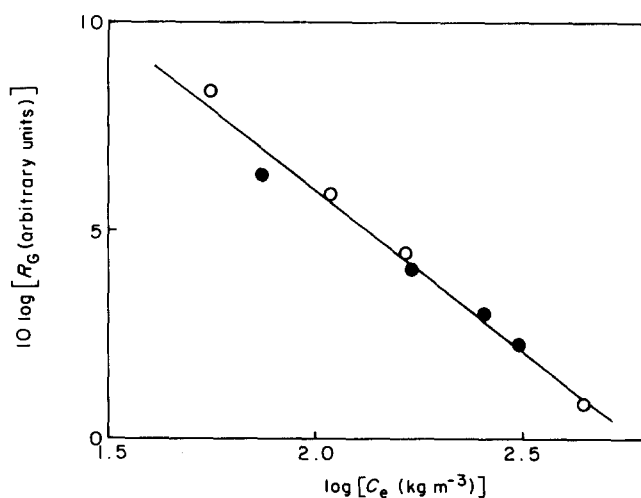
$$R_G \sim C_e^{-0.760} \quad (12)$$

In calculating  $R_G$  by using (11), even if  $M_c$  determined from (3) is employed, the expressed as indicated by (12) will remain unaltered except for changes of numerical coefficient because  $M_c$  was proportional to  $M_n$ . Comparing (6) and (12), one finds that the exponents are approximately equal, exclusive of numerical coefficient, and thus  $\zeta$  corresponds to  $R_G$ , as the  $C^*$  theorem points out. Therefore,  $\zeta$  can be replaced by  $R_G$  in (8):

$$a_H \sim R_G^m \quad (13)$$

Consequently, it is apparent from equation (13) that  $a_H$  (which depends on  $C_e$ ) can reflect the mesh size or the three-dimensional network structure in swollen gels, and that the exponent  $m$  is dependent upon the experimental conditions such as the inhomogeneity of network structure and the interaction between rubber polymer and solvent<sup>1-3</sup>. The exponent  $m$  in equation (13) will be qualitatively discussed below.

In *Figure 6* the difference in plots of  $\log a_H$  vs.  $\log C_e$  between unimodal and bimodal PDMS networks is very similar to that between undegraded networks and degraded ones as shown in *Figure 8*<sup>1-3</sup>. Although the structure of degraded networks seems to be essentially different from the bimodal network structure in *Figure 3b*, both of them commonly have the wider distribution of mesh size. Probably, by analogy with degraded networks, a 'non-frozen benzene area' formed around the network chains in smaller mesh may first prevent the crystallization of benzene, and it follows that smaller crystals grow in bimodal networks<sup>1</sup>. As a result, the crystallization temperature is reduced more sharply. The origin of large FPD for swollen gels must be essentially revealed in order to explain the difference as shown in



**Figure 7** Plots of  $\log R_G$  vs.  $\log C_e$  for unimodal (○) and bimodal (●) PDMS networks.  $R_G$  is the radius of gyration of a network chain in the swollen state, and was determined by equation (11)

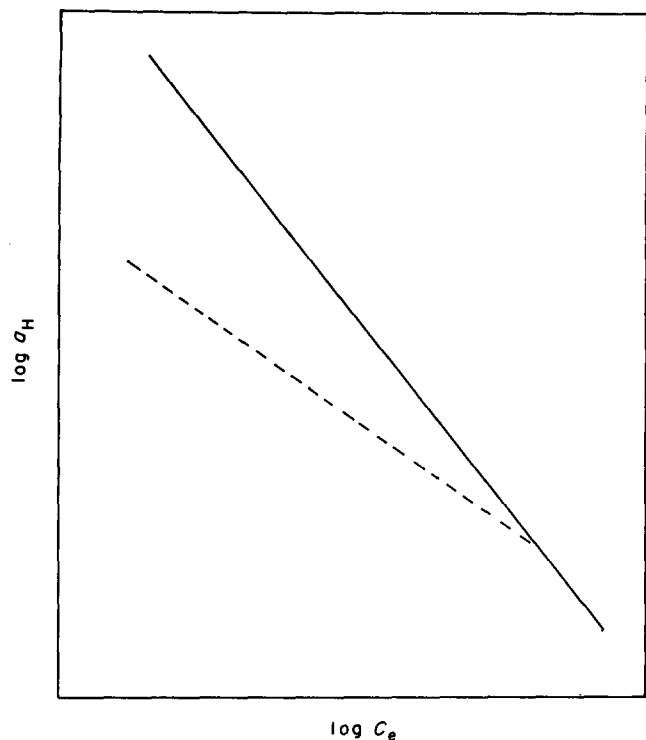


Figure 8 Scheme of the relationship between  $\log a_H$  and  $\log C_e$  for undegraded (—) and degraded (---) rubber vulcanizates

Figures 6 and 8. However, it seems to be reasonable to speculate that the large FPD for degraded networks and bimodal ones occurs because of the smaller mesh in more inhomogeneous networks compared with undegraded and/or unimodal networks.

Finally, the difference in FPD between NR solutions and PDMS ones in Figure 4 is considered to be related to the  $\chi$  parameter<sup>19</sup>. The smaller  $\chi$  is, the larger  $\Delta T$  becomes even at the same concentration of polymer solutions. This phenomenon is similar to the case of vulcanized SBR as described in the Introduction. The dependence of  $\Delta T$  on average molecular weight is also being investigated in the case of polymer solutions. The origin of FPD for polymer solution and swollen gels will be described elsewhere.

## CONCLUSION

It was experimentally confirmed by using PDMS model network that  $a_H$  corresponds to the mesh size in swollen three-dimensional network structure.

The parameter  $a_H$  could reflect the inhomogeneity of the network structure, which could not be detected by a conventional mechanical method such as stress-strain measurement.

The relationship between the plots of  $\log a_H$  vs.  $\log C_e$  for unimodal PDMS networks and those for bimodal ones was extremely similar to that between undegraded networks and degraded ones. The cause is probably due to more inhomogeneous network structure for degraded networks or for bimodal ones compared with unimodal and/or undegraded networks.

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