

Studies of the network structure of rubber vulcanizates by a cryoscopic method: 1

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The freezing-point depression, ΔT , of swollen dicumene peroxide cured natural rubber in benzene has been measured. The parameter a_H , introduced by Kuhn, which varies inversely as ΔT , should be regarded as an indication of the depression. The anomalous depression is considered to occur due to a non-frozen benzene area formed on the surrounding network chains. From comparison of the scaling law and the experimental results, it was clear that a_H can reflect not only the quantity corresponding to network chain density determined by conventional methods but also the difference in three-dimensional network structure between degraded and undegraded rubber vulcanizates.

Keywords Freezing-point depression; degradation; scaling concept; spin-spin relaxation time; rubber vulcanizates

INTRODUCTION

Recently, a new theory of rubber elasticity has been put forward by Flory *et al.*¹⁻³. The final purpose of these studies is a quantitative description of rubber elasticity on the basis of network structure.

In contrast, the network structure of ordinary rubber vulcanizates is too complex to be elucidated. The network structure of a vulcanized rubber could not be related directly to its macroscopic properties. It can be presumed from various experimental results that a real network structure is inhomogeneous: there is a molecular weight distribution of network chains between crosslinkages; trapped entanglements occur during the crosslinking process; etc.⁴. Thus far such inhomogeneity of network structure has not been essentially understood. In particular, we can only estimate the change of network structure such as scission or crosslinking along main chains by mainly chemorheological studies under the present conditions⁵.

Now, it has long been known that an anomalous freezing-point depression of the swelling solvent in swollen gels was observed, and that the magnitude of the depression was closely related to the degree of crosslinking and/or the structure of swollen gels⁶.

In this article, the origin of such an anomalous freezing-point depression will be discussed in detail, and as a new interpretation we will attempt to apply the scaling concept to the relationship between the magnitude of freezing-point depression and the network structure of rubber vulcanizates.

EXPERIMENTAL

Material used in the present study was natural rubber (NR; Pale crepe No. 1). The crosslinked rubber was prepared by milling DCP (dicumene peroxide) with uncrosslinked NR followed by pressing at 145°C and 200 kg cm⁻² for given intervals. Preparation of samples is

summarized in Table 1. All the samples were extracted with hot acetone for 48 h and dried *in vacuo*.

A degraded sample was immersed in benzene for 24 h at room temperature and dried *in vacuo*. The sol fraction was determined by the weight loss of the degraded sample. The relative network chain density, $v(t)/v(0)$, of a degraded sample was calculated from the value of the sol fraction by using Horikx's equation⁷.

The sample from which the soluble part of rubber (sol) has already been removed by the above method was also swollen in benzene for 24 h at 30°C. The equilibrium degree of swelling, Q , was determined from the increment of the weight of the swollen rubber sample, and the network chain density, $v_e(t)$, was obtained from Q by using the Flory-Rehner equation⁸. The value of interaction parameter between the polymer and solvent is 0.38.

The measurement of the freezing point was carried out as mentioned below. A swollen sample was speared on the CA thermocouple junction, and sealed up into a small glass vial. The vial contained a little benzene so that the vapour space was saturated with benzene. The apparatus used for the freezing-point determination is shown in Figure 1. The rate of cooling was *ca.* 1.0 deg min⁻¹.

Pulsed n.m.r. used to measure the spin-spin relaxation

Table 1 Preparations of natural rubber vulcanizates

| Sample no. | DCP ^a (phr ^b) | Curing time (min) | 10 ν_e (mol dm ⁻³) |
|------------|--------------------------------------|-------------------|------------------------------------|
| 1 | 2 | 10 | 0.447 |
| 2 | 2 | 20 | 0.609 |
| 3 | 2 | 30 | 0.924 |
| 4 | 3 | 20 | 1.33 |
| 5 | 3 | 30 | 1.57 |
| 6 | 3 | 40 | 1.73 |
| 7 | 3 | 50 | 1.83 |

^a Dicumene peroxide

^b Parts per hundred rubber

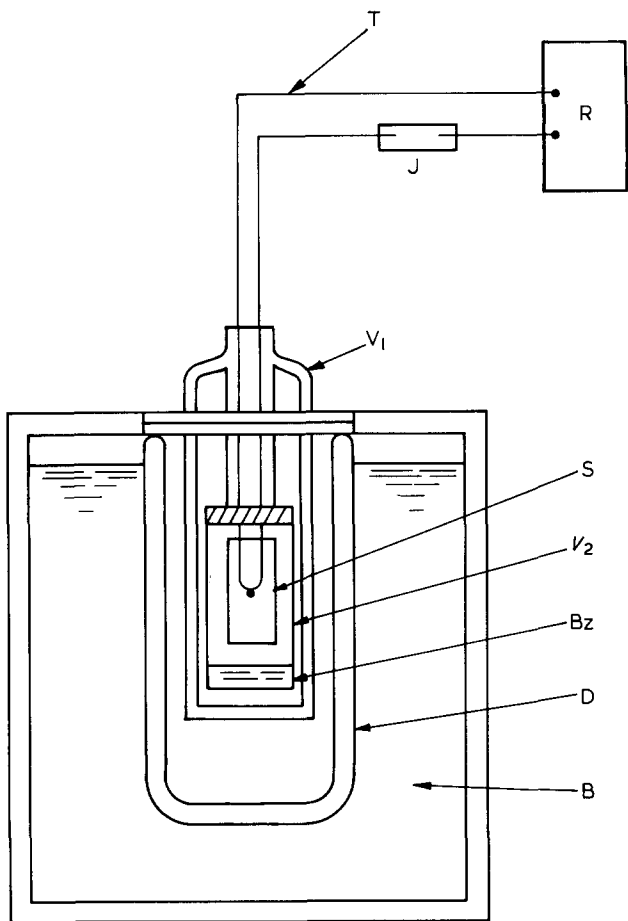


Figure 1 Sketch of the apparatus for measuring freezing point: B, dry-acetone bath; Bz, benzene; D, Dewar vessel; J, cold junction; R, recorder; S, sample; T, thermocouple; V, glass vessels

time, T_2 , was Bruker-CXP type with a proton resonance frequency of 90 MHz. The pulse sequence was $90^\circ_x, \tau, 90^\circ_y$ (solid echo pulse sequence)⁹. The width of 90° pulse and τ -value were $1.5 \mu\text{s}$ and $10 \mu\text{s}$, respectively. The samples to be measured were placed in the probe at the correct temperature and left for 20–30 min to ensure equilibrium. T_2 was calculated from the signal strength of solid echo as described elsewhere⁹.

RESULTS AND DISCUSSION

Relationship between the magnitude of freezing-point depression and network chain density, and its origin

The phenomenon of freezing-point depression occurs on the basis of the colligative effect in a usual diluted solution. In contrast, it is well known that the freezing points of aqueous gel of polyacrylic acid or poly(vinyl alcohol) and rubber vulcanizates swollen in benzene are anomalously depressed⁶.

Figure 2 indicates the freezing point of benzene, T_m , in swollen rubber vulcanizates. T_m was remarkably depressed with increasing volume fraction of rubber, v_r . Further, the magnitude of the depression is much larger than that of NR solution of benzene at the same volume fraction. Moreover, T_m for swollen samples are largely depressed even at the lower volume fraction of rubber corresponding to the dilute region as shown in Figure 2. The reproducibility of the values of T_m for swollen samples is poor, since samples are largely swollen at v_r less than 0.1.

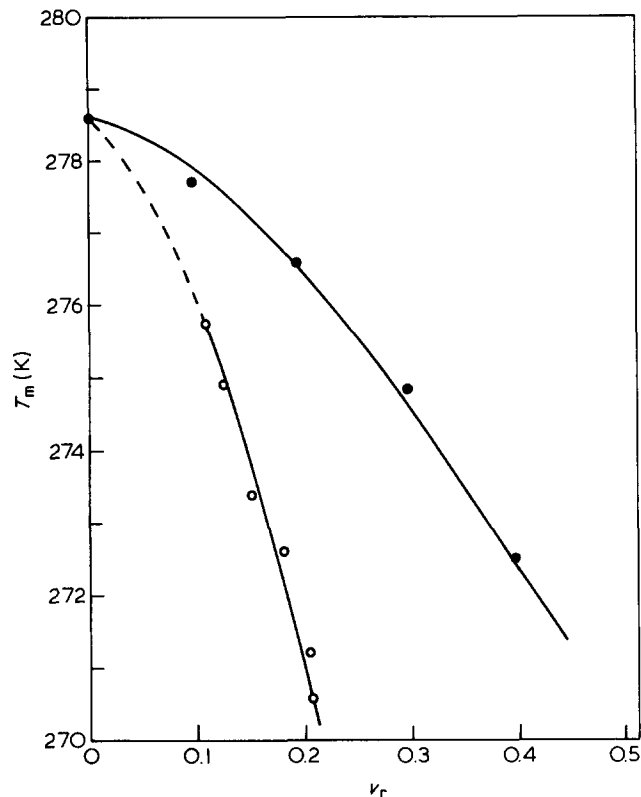


Figure 2 The dependence of the freezing points on the volume fraction of rubber for NR solution of benzene (●) and for swollen DCP-cured NR (○)

So, most probable values of T_m are indicated by the broken line in Figure 2. Such an anomalous depression for swollen samples cannot be explained only by the colligative effect of solvent molecules: the existence and/or the structure of network (or gel) must contribute to the anomalous freezing-point depression. The origin of the depression will be discussed in detail below.

Kuhn has paid attention to such a phenomenon, and equation (1) was derived on the assumption that a crystal in the gel has a higher vapour pressure than that out of the gel¹⁰:

$$a_H = -\frac{4 \times 10^3 E_m \sigma_{\text{cryst,liq}} f_c}{\rho_{\text{cryst}} R T_0 \Delta T} \quad (1)$$

where a_H = crystal size, E_m = molecular freezing-point depression, $\sigma_{\text{cryst,liq}}$ = interfacial tension between the crystal and its melt, ρ_{cryst} = density of the crystal, R = gas constant, T_0 = normal freezing temperature, ΔT = freezing-point depression, f_c = structure factor of the crystal.

a_H is referred to as a parameter of 'crystal size'. It was imagined that a_H is almost equal to the root-mean-square distance between crosslinkages in swollen gel. Thus, the size of the crystal grown in the gel was considered to be limited in size by the 'mesh' width of network¹⁰.

Now, equation (1) can be simplified to the following equation, if the swelling solvent is benzene and the structure factor of the crystal is unity:

$$a_H = -35/\Delta T \quad \text{nm} \quad (2)$$

where $E_m = 5.12 \times 10^{-3} \text{ kg K mol}^{-1}$, $\sigma_{\text{cryst,liq}} = 4.0 \times 10^{-3} \text{ J m}^{-2}$, $f_c = 1$, $\rho_{\text{cryst}} = 1.01 \times 10^{-3} \text{ kg m}^{-3}$, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T_0 = 278.5 \text{ K}$, respectively. But the value of a_H is

considerably different from the crystal size determined by X-ray diffraction¹¹.

However, since ΔT is greatly dependent on the degree of crosslinking as shown in Figure 2, a_H should be regarded as an 'indication' which varies inversely as ΔT and may be associated with the structure of network or gel.

Figure 3 shows the dependence of a_H on Q and v_e . a_H decreased with increasing v_e , and the degree of decreasing of a_H becomes lower in the range $v_e \geq 1.0 \times 10^{-4}$ mol dm^{-3} . a_H , however, may be a reliable indication in evaluating degradation such as scission along main chains. Further, the value of a_H can be extrapolated to be zero at $Q=0$ within the experimental errors as shown in Figure 3. Thus, $Q=0$ corresponds to an unswollen state or to an extremely high network chain density. Since the crystals of benzene do not naturally exist in the gel under such a condition, the above relationship can be considered to be reasonable.

Next the origin of such an anomalous freezing-point depression will be discussed below.

Figure 4 indicates the variations of ΔT with the number-

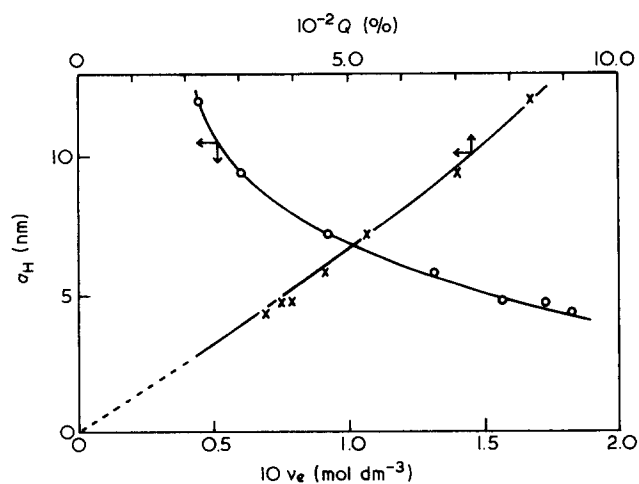


Figure 3 The relationship between the crystal size, a_H , the equilibrium degree of swelling, Q , and the network chain densities, v_e , for undegraded DCP-cured NR samples

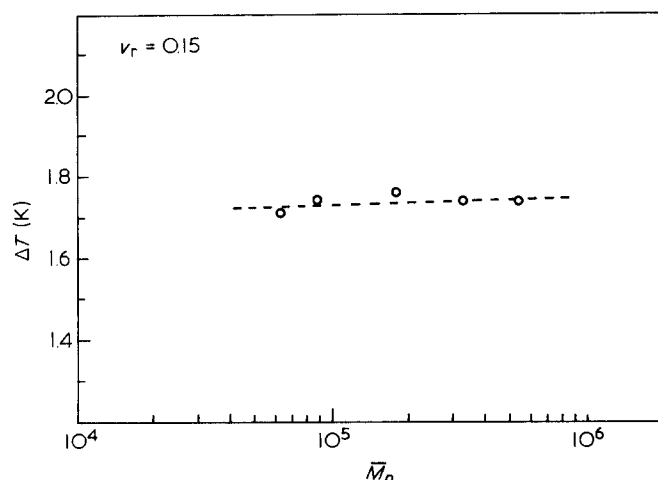


Figure 4 The changes of freezing-point depression, ΔT , of NR solution of benzene with the number-averaged molecular weight of rubber. v_r indicates the volume fraction of rubber in benzene

averaged molecular weight, \bar{M}_n , of NR under the condition of a constant volume fraction of rubber in benzene solution ($v_r=0.15$). ΔT was independent of \bar{M}_n , and ΔT changes with v_r , as shown in Figure 2 even if the number of moles of rubber in benzene are constant. It follows that the origin of the depression cannot be explained only by the colligative effect. In addition, in Figure 4 the dynamic entangled network structure is expected to be formed in the region of higher molecular weight. However, since ΔT was almost constant, such an entangled network structure is probably thought not to contribute mainly to the freezing-point depression for swollen rubber vulcanizates or for concentrated rubber solution.

So, the spin-spin relaxation time of proton nuclear magnetic resonance, T_2 , was measured in order to evaluate the mobility of network chains in both swollen and dry rubber vulcanizates as shown in Figure 5. The measurement of T_2 was carried out in the range of room temperature down to 200K. Since intermolecular spin-spin interactions decrease in the swollen state, the dependence of T_2 on temperature for swollen samples should not be directly compared with that for dry samples.

Now, the temperature range in which the crystallization of benzene in swollen samples has apparently been complete is shown in Figure 5. The value of T_2 in this range of temperature suggests that network chains are still thermally mobile in the crystal field of benzene. On the other hand, benzene has great affinity for natural rubber.

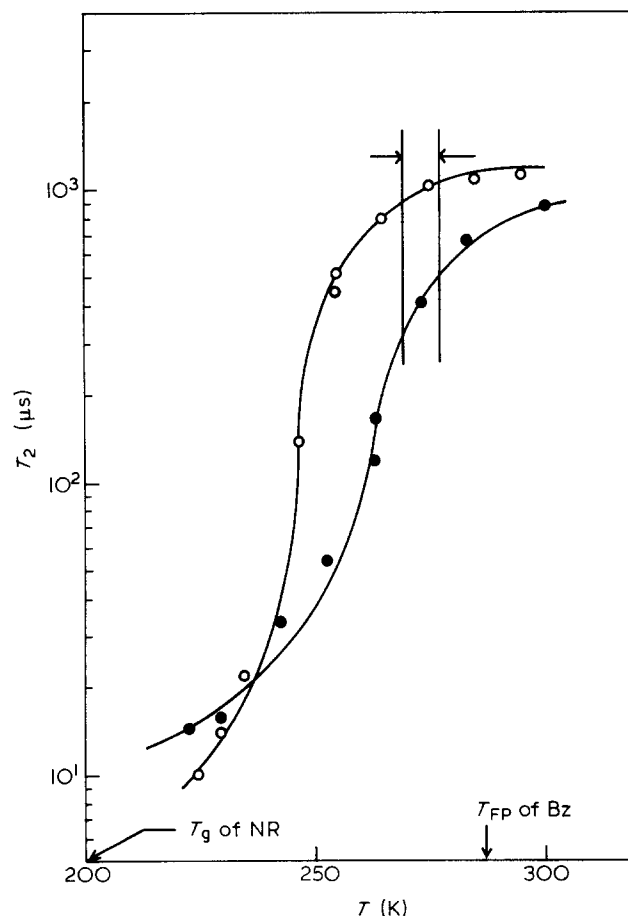


Figure 5 T_2 dependence of temperature for dry (●) and swollen (○) samples. Benzene in swollen samples crystallizes in the range of temperature illustrated by the two arrows

It follows that the network chains are solvated by benzene molecules, a system which is in more energetic motion than the pure benzene. Probably, a 'non-frozen benzene area' where the crystal lattice of benzene may be disordered by the motion of network chains is considered to be formed around the network chains in swollen samples. Because of this area, benzene has less tendency to crystallize, and it follows that the crystallization temperature is reduced sharply. The existence of a network in rubber vulcanizates probably lets the crystals of benzene be bordered by the above area. However, the size of the bordered crystals is not necessarily equal to the mesh size of the network, because the non-frozen benzene area is not similarly formed around each of the network chains, since the formation of the area is governed by the mobility and the configurations of network chains in swollen rubber samples, which is supported by the fact that the observed spin echo did not decay exponentially in the above temperature range^{9,12}.

The mobility of network chains is essentially determined by a kind of rubber and the degree of crosslinking. Therefore, a_H (or ΔT) depends on v_e as shown in Figure 3. The mobility of benzene molecules in swollen network and NR solution will be measured by using pulsed n.m.r. in the future to make clear non-frozen benzene area.

Application of the cryoscopic method to degradation

Figure 6 shows the relative changes of a_H , $a_H(0)/a_H(t)$, as degradation proceeds. The DCP-cured NR was degraded at 110° and 120°C in air. The relative changes of a_H corresponded well to those of the degree of degradation determined by the swelling and sol fraction method. The degree of degradation measured by the swelling method was lower than that by the other methods in the case of extreme degradation because, since samples are much damaged in such a stage, the experimental errors may become larger in measuring the equilibrium degree of swelling. In contrast, the freezing point can be measured regardless of the shape of a degraded sample in the present method.

Figure 7 indicates the comparison of a_H for undegraded samples with various network densities and that for degraded samples at 110°C in air. a_H for degraded samples was always lower than that for undegraded ones. This tendency was similar to that at 120°C in air. There are still

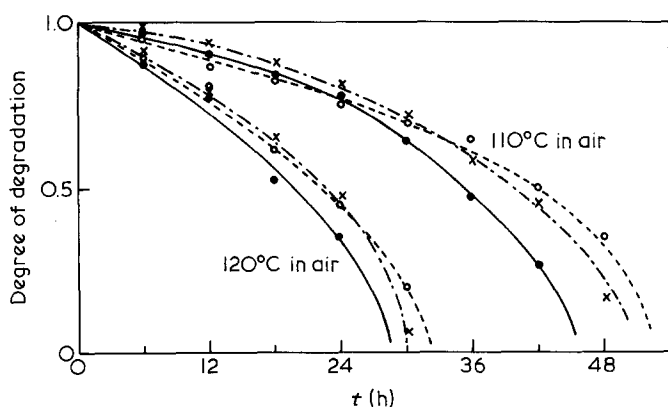


Figure 6 Comparison of $a_H(0)/a_H(t)$ (○) and the degree of degradation determined by other methods: the swelling method, $v_e(t)/v_e(0)$ (●); the sol fraction method, $v(t)/v(0)$ (X)

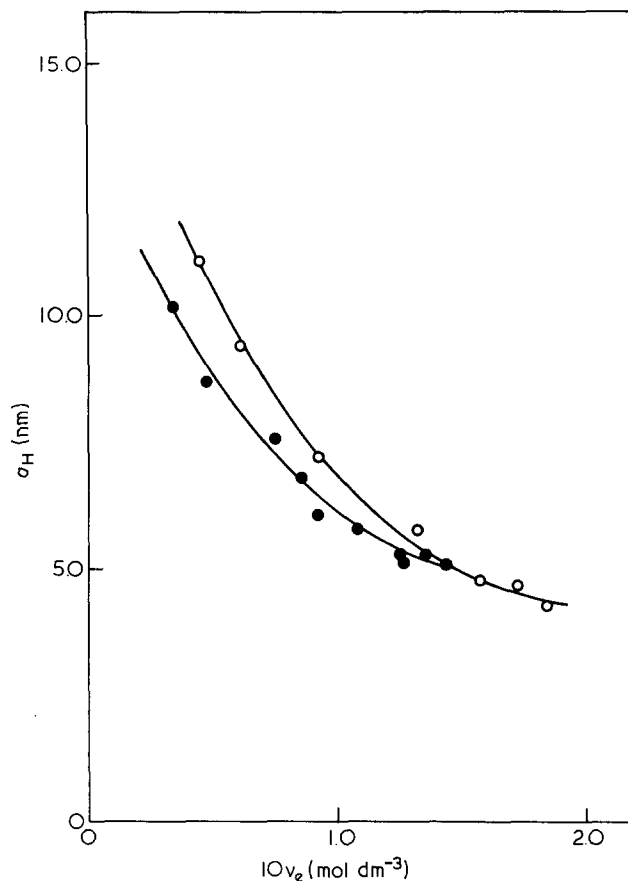


Figure 7 Comparison between the changes of a_H for an undegraded rubber (○) and that for a degraded one (●)

the survived smaller mesh and star-shaped dangling chains in a degraded network. The non-frozen benzene area surrounding the network chains in the survived smaller mesh may first prevent the crystallization of benzene, and it follows that smaller crystals grow in the survived mesh. Further, the dangling chains are so flexible that they may disturb the crystal lattice of benzene.

Anyhow, it is evident that a_H can reflect not only the quantity corresponding to the network chain density or to the degree of degradation determined by conventional methods but the difference in three-dimensional network structure between a degraded and an undegraded network.

However, a_H is only an indication, and the difference in a_H between degraded and undegraded rubber vulcanizates with apparently the same network chain densities is not revealed in Figure 7. So, the comparison of the scaling concept and the experimental results in the present study was attempted in order to give a_H physical meaning¹³. Equation (3) derived by de Gennes indicates the relationship between concentration, C , in semi-dilute polymer solutions and the screening length, ξ ¹⁴:

$$C = M_\xi / \xi^3 \tag{3}$$

where ξ corresponds to the root-mean-square distance between dynamic entanglements of polymer chains of semi-dilute solutions in a good solvent. M_ξ is the molecular weight associated with ξ and expressed by¹⁴:

$$M_\xi \propto \xi^{5/3} \tag{4}$$

For networks in the equilibrium swollen state, equation

(3) still holds if one replaces C by C_e ¹⁵:

$$C_e \approx M_c / \xi^3 \quad (5)$$

where C_e is the concentration of polymer of the swollen samples at the equilibrium swelling. The validity of equation (5) was experimentally confirmed¹⁶. One can derive the following equation given by:

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

Figure 8 shows the plots of $\log a_H$ vs. $\log C_e$ on the basis of the experimental results in Figure 7. It is apparent that an approximately linear relationship exists between $\log a_H$ and $\log C_e$ in any case. The dependence of a_H on ξ was obtained from equation (6) and the slope of the graph in

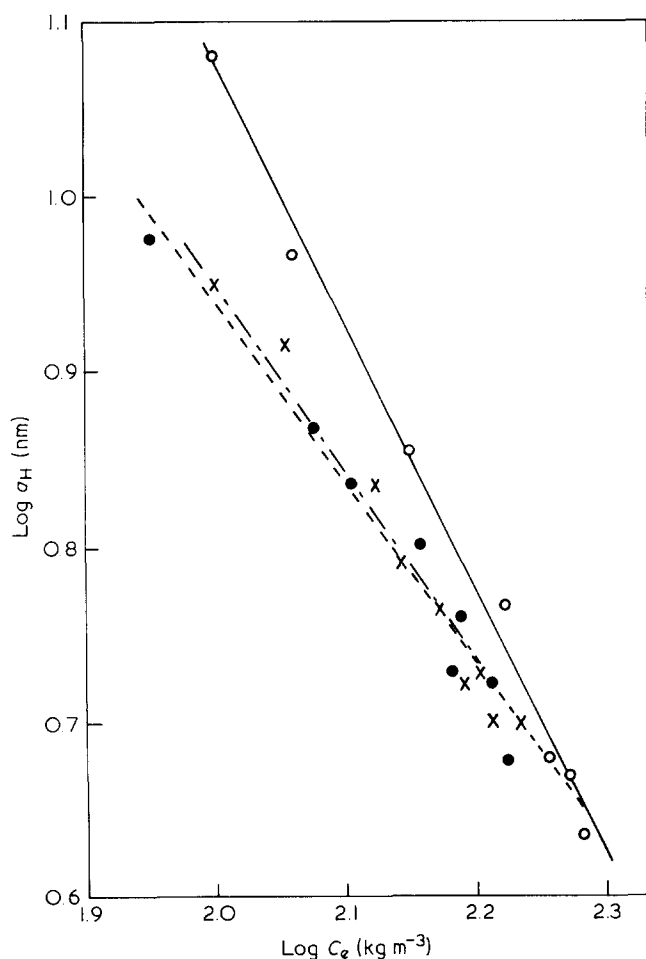


Figure 8 Plots of $\log a_H$ vs. $\log C_e$ for DCP-cured NR. C_e is the swelling equilibrium concentration of polymer in the swollen networks: (O) undegraded samples; (●) degraded samples at 110°C in air; (X) degraded samples at 120°C in air

Figure 8:

$$a_H \propto \xi^{2.0} \quad \text{for an undegraded network} \quad (7)$$

$$a_H \propto \xi^{1.3} \quad \text{for a degraded network} \quad (8)$$

ξ can be regarded as the radius of gyration of the network chains between crosslinks¹³. ξ generally becomes larger as the network chain density decreases. Equations (7) and (8), however, imply that the three-dimensional spatial situation or structure of a degraded network is different from that of an undegraded network. Thus, the network structure for an undegraded sample is essentially alternative to that for a degraded one, even if both of them have apparently the same network chain densities¹⁷. Such a difference could not so far be found by any other methods or approaches.

In the future, the origin of the anomalous freezing-point depression will be further pursued in detail, and this cryoscopic method will be applied to the alternative types of degradation, i.e. scission at or near the crosslinkages and interchange in polysulphide in sulphur-cured rubber.

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