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Dynamic Light Scattering of Swollen Rubber Vulcanizates and the Swelling Mechanism

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ABSTRACT: Dynamic light scattering (DLS) could be measured for end-linked poly(dimethylsiloxane) (PDMS) model networks and ordinary rubber vulcanizates such as dicumyl peroxide (DCP)-cured natural rubber (NR), and the cooperative diffusion constant D_{coop} was determined. The validity of the so-called C* theorem was experimentally confirmed by comparison of D_{coop} for PDMS solutions with that of swollen PDMS networks. Variations of D_{coop} with cross-link density for both PDMS networks and DCP-cured NR approximately corresponded to the prediction expected from both the dynamic scaling law and the C^* theorem. The relationship between D_{coop} and number-average molecular weight M_n of PDMS prepolymers also nearly obeyed the dynamic scaling law, and the average distance between cross-link sites in swollen PDMS networks at the equilibrium state of swelling, which was estimated from M_n of PDMS prepolymers, was in good agreement with the correlation length ξ calculated from D_{coop}. It follows that ξ can be regarded as the mesh size of a swollen network. As a result, an average molecular weight between cross-link sites for PDMS networks determined from the application of the C^* theorem, which value was approximately equal to M_n of PDMS prepolymers, was suggested to be reasonable, while the same quantity derived from the conventional Flory–Rehner equation (FR equation) was found to be at least overestimated at (much) lower cross-link densities. These facts imply that the basic assumption of affine deformation in the FR equation is not applicable to such networks. Further, it has become apparent from DLS measurements for swollen DCP-cured NR that trapped entanglements are nearly equivalent to chemical cross-link sites at the equilibrium state of swelling.

Introduction

Recently, many kinds of hydrogels have been widely investigated as a functional material,[1] since volume phase-transition phenomena of swollen gels were theoretically and experimentally found by Dušek and Prins[2] and Tanaka et al.[3,4] However, the relationship between network structure of gels and mechanical properties has not been satisfactorily elucidated because of the complexity of a network structure, e.g., a distribution of molecular weight between cross-links, trapped entanglements, free terminal chain ends, and other heterogeneous network structure.[5-7] Numerous discussions with respect to the theory of rubberlike elasticity for the past 10 years describe these facts.[8-13] For a cross-linked rubber, which is a representative gel, an average molecular weight between cross-link sites M_c, which is one of the most important structural parameters and characterizes a network structure, has been already determined by means of two techniques:[14] (1) M_{c1}, the use of the conventional Flory–Rehner equation (FR equation);[15] (2) M_{c2}, the application of the C^* theorem, which was proposed by de Gennes.[16] The FR equation is usually adopted to calculate the cross-link density of a cross-linked rubber. The C^* theorem suggests that the swelling of the network chains in a good solvent is the same as that of equivalent chains at infinite dilution in the same solvent and that the equilibrium concentration of polymer in the swollen cross-linked polymer can be identified with the so-called crossover concentration between dilute and semidilute regions of polymer solutions of the same molecular weight as the strands in the network. The validity of this assumption has been evidenced in the first approximation by some small-angle neutron scattering (SANS) experiments.[13,17] Cross-linked polymers used in our previous paper[14] were an end-linked poly(dimethylsiloxane) (PDMS) model network and dicumyl peroxide (DCP) cured natural rubber (NR, pale crepe no. 1). There M_{c1} agreed fairly with M_{c2} at high cross-link densities for both kinds of samples, but M_{c1} became larger than M_{c2} as the cross-link density decreased. The values of M_{c1} for DCP-cured NR having much lower cross-link densities seemed to be unrealistic when compared with the average primary molecular weight for the same un-cross-linked NR. On the other hand, M_{c2} for PDMS networks was in agreement with the number-average molecular weight M_n for PDMS prepolymers. These facts mean that the application of the C^* theorem may be more valid than the FR equation at lower cross-link density and that the swelling mechanism of such a network may be nonaffine,[13] which is entirely different from the basic assumption in the FR equation. This corresponds to a series of experimental results of SANS measured by using partially deuterated model networks[18,19] and to the rearrangement model of the spatial cross-link sites explained by Bastide et al.[20]

In this article, the network mesh size in a network of a cross-linked rubber swollen at the quilibrium state of swelling will be attempted to be estimated by use of the dynamic light-scattering (DLS) technique,[21] and the swelling mechanism will be discussed in detail. Some DLS studies have been already carried out for polyacrylamide gels and polystyrene gels.[3,4,22-24] However, there were no DLS experiments on "ordinary" rubber valcanizates.

Experimental Section

A. Sample Preparation. Cross-linked polymers used in the present study were end-linked PDMS model networks and DCP-cured NR. Preparations and characterization of all samples were described elsewhere.[14] Benzene (Bz) was used as a (swelling) solvent.

B. DLS Instrument and Measurements. Figure 1 shows a diagram of the DLS apparatus. The optical system that utilized the polarization microscope has been designed and constructed so that the scattering angle θ was fixed at 90°. A homodyne spectrometer was employed using 0.2-mm-diameter pinholes.[21]

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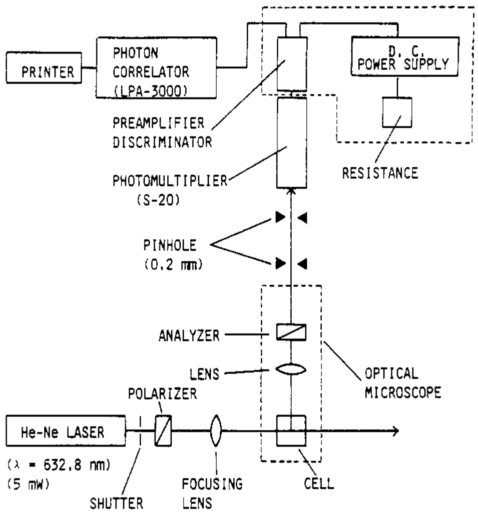

Figure 1. Diagram of the dynamic light-scattering (DLS) instrument.

The distance between two pinholes R must satisfy the following relation:[21]

$$nd^2 < \lambda R \tag{1}$$

where d and λ are the diameter of the pinhole and the wavelength of the incident laser beam (λ = 632.8 nm), respectively. n is a constant and was assumed to be unity. The photon correlator is a LPA-3000 (Ootsuka Electronics Co., Ltd.), and the photon correlation was measured by the time-interval method:[25] the clock rate was 20 μs; the number of channels was 256; the accumulation was 100 times. All measurements were carried out at 293.15 K in a clean room.

Dust was removed from Bz solutions of PDMS with a fluoropore filter (Sumitomo Electric Ind., Ltd.), having 0.45-μm pore size. A cross-linked rubber was swollen in the quartz cell containing excess Bz up to the equilibrium state of swelling, and dust in swollen samples was eliminated as much as possible by several times exchanging Bz in the cell for dust-free Bz, which had been already purified with the above filter. All samples were allowed to stand for at least 1 day to attain stability.[23] This could be checked by monitoring the strength of scattering light. Further, the LPA-3000 has a "dust-cutting" function by which the correlator does not count photon pulses in case that the number of photons per one clock is 5% more than the average value, which has been previously determined from the first 10 accumulation times of measurements.

C. Analysis of Data. The normalized second-order intensity autocorrelation function of photoelectric current $|g^{(2)}(\tau)|$ is expressed by[26]

$$|g^{(2)}(\tau)| = 1 + \beta|g^{(1)}(\tau)|^2 + \delta \quad (\delta \ll 1) \tag{2}$$

where $|g^{(1)}(\tau)|$ and τ are the normalized first-order intensity autocorrelation function of photoelectric field and the correlation time, respectively. If the fluctuation of the electric field is assumed to be a Gaussian distribution, the constant β in eq 2 is unity.[26] However, the value of β is actually an instrumental factor and is less than unity owing to the incoherence of the photomultiplier.[27] In particular, β becomes small in case of swollen gels.[23,28] δ in eq 2 is the deviation from the baseline. If the fluctuation of concentration in polymer solutions and/or in swollen gels may be thermally random, $|g^{(1)}(\tau)|$ decreases exponentially by the decay constant Γ, and the translation self-diffusion constant D_0 of polymers and/or the cooperative diffusion constant D_{coop} of swollen cross-linked polymers are theoretically given by[29]

$$|g^{(1)}(\tau)| = \exp(-\Gamma\tau) = \begin{cases} \exp(-q^2 D_0 \tau) \\ \exp(-q^2 D_{\text{coop}} \tau) \end{cases} \tag{3}$$

where q indicates the scattering vector, which is represented by λ, θ, and the refractive index of the (swelling) solvent (Bz: n_0 = 1.4703 at 293.15 K):[29]

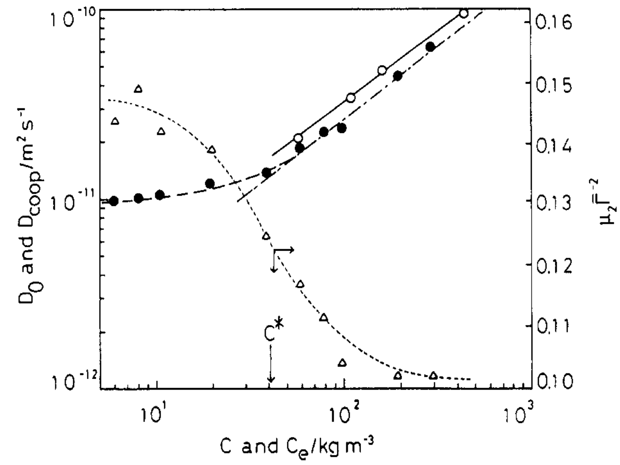

Figure 2. Variations of the translation self-diffusion constant D_0 (●) and of the normalized deviation $\mu_2\bar{\Gamma}^{-2}$ (△) determined by the cumulant method for benzene (Bz) solutions of poly(dimethylsiloxane) (PDMS), whose number-average molecular weight M_n is 5.5×10^4, and the dependence of cooperative diffusion constant D_{coop} (○) for end-linked PDMS networks swollen in Bz on polymer weight concentration at the equilibrium state of swelling C_e. C^* means the calculated crossover concentration of PDMS solutions.

$$q = (4\pi n_0/\lambda) \sin (\theta/2) \tag{4}$$

The deviation of $|g^{(1)}(\tau)|$ from a single-exponential decay was analyzed by the second-order cumulant method as expressed by[30]

$$\ln [\beta^{1/2}|g^{(1)}(\tau)|] = \ln \beta^{1/2} - \bar{\Gamma}\tau + 1/2(\mu_2/\bar{\Gamma}^2)(\bar{\Gamma}\tau)^2 \tag{5}$$

where $\bar{\Gamma}$ and $\mu_2\bar{\Gamma}^{-2}$ are respectively the averaged decay constant of Γ and the normalized variance, which are defined by the distribution function of Γ, $G(\Gamma)$:

$$\bar{\Gamma} = \int \Gamma G(\Gamma)\, d\Gamma \tag{5'}$$

$$\mu_2 = \int (\Gamma - \bar{\Gamma})^2 G(\Gamma)\, d\Gamma \tag{5''}$$

The correlation length ξ was calculated from the following relation, which is the same type as the Stokes–Einstein equation:[16,29]

$$\xi = k_B T/(6\pi\eta_0 D_{\text{coop}}) \tag{6}$$

where k_B, T, and η_0 are the Boltzmann constant, the absolute temperature, and the viscosity of a (swelling) solvent (Bz: η_0 = 0.652 m Pa s), respectively. The dependence of η_0 on concentration was assumed to be negligible.[31]

All experimental results in the present study have satisfied the following requirement: $q\xi < 1$.[32] In the preliminary experiment of DLS, the particle size of the standard monodisperse polystyrene latex (Dow Chemical Co.) could be determined by using eq 6, in which ξ is equal to half the particle size,[29] within the experimental error of ca. 1%. The systematic errors of the value of $\bar{\Gamma}$ on calculation of the cumulant analysis were approximately 5–10%.

Results and Discussion

A. DLS of Polymer Solutions. Figure 2 indicates the dependence of D_0 and $\mu_2\bar{\Gamma}^{-2}$ on polymer concentration C for PDMS solutions and also shows the variations of D_{coop} for PDMS networks with polymer weight concentration at the equilibrium state of swelling C_e. PDMS with $M_n = 5.5 \times 10^4$ is the same as that of the prepolymer of the end-linked PDMS network with the lowest cross-link density. The symbol C^* displays the so-called crossover concentration of PDMS solutions in the same figure,[16] the detail explanation for which is described in

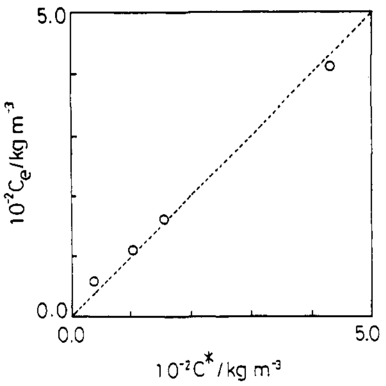

Figure 3. Comparison of measured C_e for swollen PDMS networks with calculated C^* for PDMS prepolymer solutions.

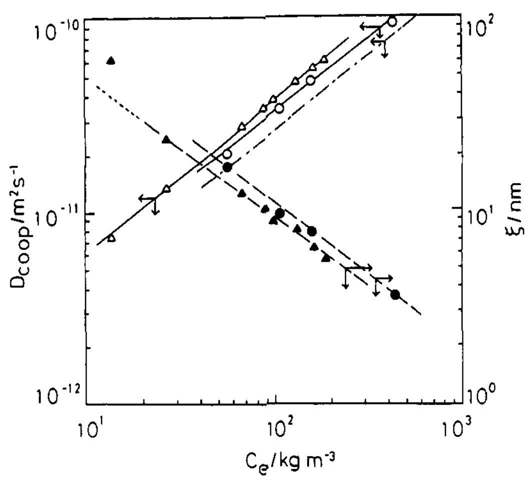

Figure 4. Dependence of D_{coop} on C_e for PDMS networks (○) and for dicumyl peroxide (DCP) cured natural rubber (NR) (△), and the plots of the correlation length ξ estimated from D_{coop} vs C_e for PDMS networks (●) and for DCP-cured NR (▲). The one-dotted line represents D_{coop} for PDMS solutions, which are the same data shown in Figure 2.

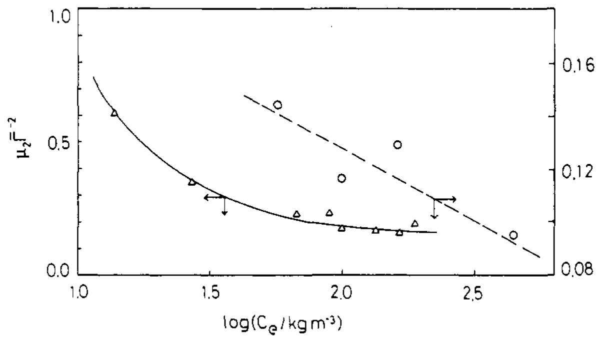

Figure 5. Relationship between $\mu_2\bar{\Gamma}^{-2}$ and C_e for PDMS networks (○) and for DCP-cured NR (△).

ref 14. In the present study, the polymer concentration was not so low ($C \sim 10^0$ kg m^{-3}) and the M_n of PDMS not so high that D_0 had not to be corrected by solvent-displacement factor.[33] In the dilute regime ($C < C^*$), D_0 of the individual polymer coils increased slightly with increasing C. This phenomenon is in good agreement with the decrease of the radius of gyration, which has been evidenced by SANS experiments.[34] D_0 in the dilute limit has been proved to be independent of C and constant.[35,36] In the semidilute range ($C > C^*$), D_0 increased remarkably with C and was proportional to C to the power of 0.75, as predicted by the dynamic scaling law.[16] The values of D_0 in this region are nearly consistent with those of D_{coop} for PDMS networks within the experimental error, though there is a systematic upward shift of D_{coop} relative to PDMS networks, with respect to D_0 of semidilute solutions of PDMS.[35] The dependence of D_{coop} on C_e will be quantitatively discussed in section B. Similar experimental results have been also reported for PDMS and/or polystyrene in toluene.[17,35]

The values of $\mu_2\bar{\Gamma}^{-2}$ for PDMS solutions diminished around C^* as shown in Figure 2. The individual polymer chains of PDMS are entangled and penetrated each other at $C > C^*$. A transient network, which has a finite lifetime, seemed to be formed.[16,24] The translation self-diffusion (or center-of-mass diffusion) mode associated with the displacement of the individual polymer coils is suppressed by many entanglements in a transient network, and the mean position of polymer chains is almost constant and only fluctuated in the solutions. It follows that $|g^{(1)}(\tau)|$ exhibits nearly a single-exponential decay because of a cooperative (or collective) gellike (or breath) mode already mentioned[29,36] and that $\mu_2\bar{\Gamma}^{-2}$ becomes smaller. On the other hand, in the dilute regime, $|g^{(1)}(\tau)|$ decays nonexponentially, and $\mu_2\bar{\Gamma}^{-2}$ increased through the polydispersibility of PDMS,[37] which value is ca. 1.5, and the center-of-mass hydrodynamic mode of the individual polymer chains.[38]

In a word, such a transient network behaves like a permanently cross-linked polymer. Further, the measured values of C_e for all PDMS networks were well in accord with the calculated ones of C^* for each PDMS prepolymer as shown in Figure 3. These facts suggest that validity of the C^* theorem.

B. DLS of Swollen Cross-Linked Polymers. Figure 4 indicates the relationship between D_{coop}, ξ, and C_e for PDMS networks and DCP-cured NR. The one-dotted line displays the experimental data for PDMS solutions at $C > C^*$ shown in Figure 2. D_{coop} generally increases with C_e, since the restoring force (due to the osmotic pressure in swollen (transient) networks) is stronger at high concentration, which is a reverse tendency of the translation self-diffusion constant for an ordinary solute particle.[16] The values of ξ calculated by eq 6 decreased with C_e, corresponding to changes of D_{coop}. For PDMS networks, D_{coop} and ξ were respectively proportional to C_e to the power of 0.74 and −0.76, which well satisfies the theoretical prediction expressed by[16]

$$D_{coop} \sim \xi^{-1} \sim C_e^{0.75} \qquad (7)$$

On the other hand, in case of DCP-cured NR, D_{coop} and ξ varied with C_e to the power of 0.79 and −0.73, respectively, except for the experimental data at the lowest cross-link density. This deviation is considered to be due to a large systematic error by the cumulant analysis at (much) lower cross-link densities, as described in Figure 6.[37]

For both kinds of samples, the obtained values of D_{coop} are approximately the same order as those of other swollen gels.[22-24] Here, it should be kept in mind that the dependence of Γ (or $\bar{\Gamma}$) on q, that is, the linearity of the plots of Γ (or $\bar{\Gamma}$) vs q^2, has not been investigated, because θ cannot be changed in the present work. However, the experimental condition of $\theta = 90°$ is frequently preferred in the case of DLS measurements of swollen gels because the strength of scattering light is generally weak,[23,27,28] dust in swollen gels cannot be perfectly removed,[32] and stray light on the wall of the cell and/or a mode of intramolecular motion along longer network chains at (much) lower cross-link density can be effectively negligible.[39]

Figure 5 depicts the variations of $\mu_2\bar{\Gamma}^{-2}$ with C_e. The values of $\mu_2\bar{\Gamma}^{-2}$ for PDMS networks are approximately the same as those of PDMS solutions at $C > C^*$ indicated in Figure 2, while the same quantities for DCP-cured NR

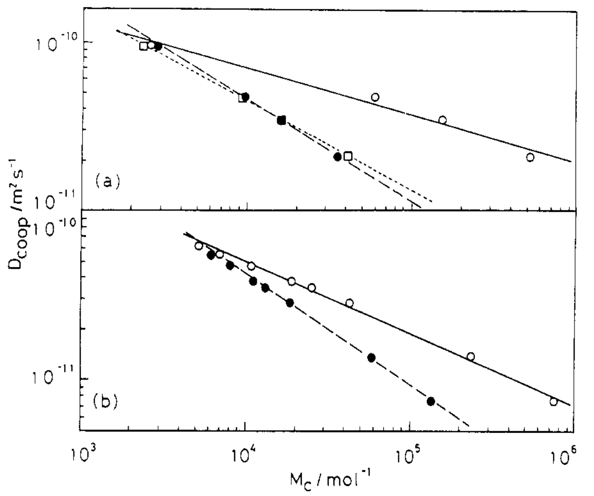

Figure 6. Plots of D_{coop} vs an average molecular weight between cross-link sites M_c: (a) PDMS networks; (b) DCP-cured NR. Open circles are M_{c1} estimated by use of the conventional Flory–Rehner equation, closed circles are M_{c2} determined from the application of the C^* theorem, and square symbols are M_n of PDMS prepolymers.

was about 0.2, even at high cross-link densities. The network structure of DCP-cured NR can be considered to have a wider distribution of M_c and to be nonhomogeneous, in comparison with PDMS networks.[23] In case of DCP-cured NR, $\mu_2\bar{\Gamma}^{-2}$ increased and became ca. 0.5 with decreasing cross-link densities.[38,40] In such a case, the systematic errors on calculation, which was made by the cumulant analysis, is anticipated to be larger.[37] The method has also been proposed to minimize the experimental error on DLS measurements by systematically changing the clock rate, when the value of $\mu_2\bar{\Gamma}^{-2}$ is predicted to be more than ca. 0.3.[37] However, a definitive dependence of $\bar{\Gamma}$ on clock rate has not been obtained in this work.

C. Swelling Mechanism of Rubber Vulcanizates. Figure 6 shows the relationship between D_{coop} and M_c for both PDMS networks and DCP-cured NR. As mentioned in the Introduction, M_{c1} was calculated by the FR equation, and M_{c2} was estimated from the application of the C^* theorem. In Figure 6a, it is first worth noting that the slope of the plots of log D_{coop} for PDMS networks vs log M_n for PDMS "prepolymers" was −0.53 and that this exponent can be considered to be close to the theoretical prediction represented by the following relation:[16]

$$D_{coop} \sim M_c^{-0.6} \tag{8}$$

M_{c2} is approximately equal to M_n,[14] and so the D_{coop} dependence on M_{c2} naturally obeys eq 8. On the contrary, since M_{c1} is much larger than M_{c2} at (much) lower cross-link densities, the slope of the plots of log D_{coop} vs log M_{c1} becomes gentle. A similar tendency was also obtained for DCP-cured NR as shown in Figure 6b.

For ordinary rubber vulcanizates such as DCP-cured NR, M_{c1} is often altered by a correction accounting for free terminal chain ends in real network at low cross-link density.[15] The corrected values of M_{c1} were apparently almost equal to M_{c2}.[14] This correction, however, cannot be carried out for PDMS networks, because one is unable to define a primary molecular weight (or a primary polymer chain) owing to an end-linking. Actually, free terminal chain ends are thought to scarecely exist in PDMS networks.[14]

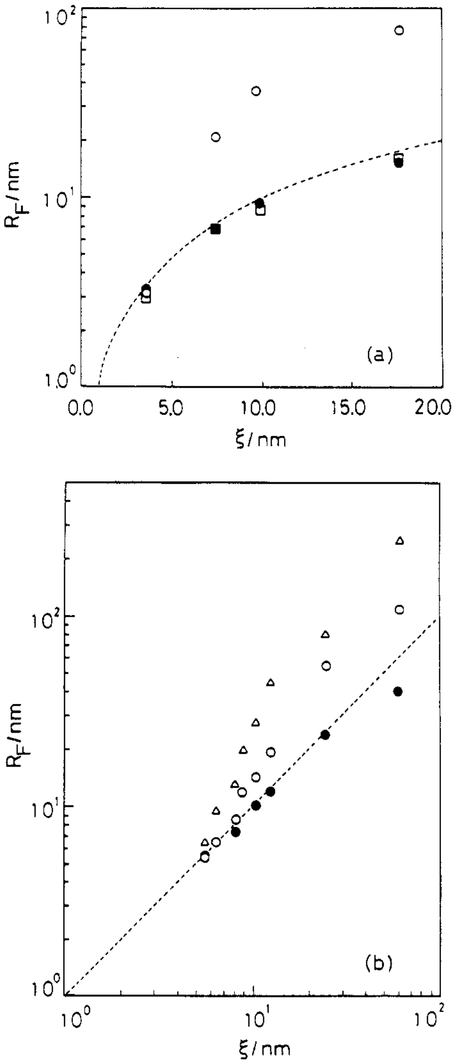

Figure 7. Comparison of average distance between cross-link sites R_F in a swollen network at the equilibrium state of swelling with ξ: (a) PDMS networks; (b) DCP-cured NR. Open circles, closed circles, and square symbols are respectively the values of R_F estimated from M_{c1}, M_{c2}, and M_n by using eq 9. R_F represented by triangular symbols are calculated from M_c between chemical cross-link sites, which was determined by measuring the sol fraction. In eq 9, a = 0.847 nm and χ = 0.484 (293.15 K, Bz) for PDMS, a = 0.620 nm and χ = 0.38 + 0.03v_r (293.15 K, Bz) for NR, where v_r is the volume fraction of rubber at the equilibrium state of swelling.

Now, R_F was calculated in practice by use of the following relation:[13,14]

$$R_F = a(0.5 - \chi)^{1/5}(M_c/m)^{\nu} \tag{9}$$

where R_F, a, χ, and m are respectively the end-to-end average distance of network chain between cross-link sites at the equilibrium state of swelling, the segment length, the interaction parameter between polymer and solvent (Flory–Huggins' constant),[15] and the molecular weight of monomer. (Numerical values of these quantities are given in the caption of Figure 7.[14])

The universal exponent for the excluded-volume effect ν in eq 9 is close to 0.6 for a good solvent. It has become easily apparent from eq 9 and D_{coop} dependence on M_{c2} shown in Figure 5 that ξ, which is inversely proportional to D_{coop} as expressed by eq 6, may correspond to a mesh size of swollen networks, and the absolute value of ξ is very interesting in order to research the swelling mechanism of a cross-linked rubber.

In Figure 7, the values of ξ were compared with those of R_F, which had been calculated by reversely substituting each value of M_{c1}, M_{c2}, and M_n in eq 9. First, $R_F(M_n)$, which was independently determined from the M_n of PDMS prepolymers, was quite consistent with the values of ξ as shown in Figure 7a. It is experimentally confirmed by this fact that ξ can be regarded as R_F in the C^* theorem or in the THB model.[41] Thus, D_{coop} has the same structure as a simple Stokes–Einstein diffusion constant for a single blob, and the mesh size of a blob may correspond to the average distance between cross-link sites in swollen networks at the equilibrium state of swelling.[16,41] For PDMS networks, $R_F(M_{c2})$ calculated from M_{c2} was similarly in good agreement with ξ because $M_{c2} \simeq M_n$.[14] The agreement between $R_F(M_{c2})$ and ξ was also found for DCP-cured NR as shown in Figure 7b. On the other hand, $R_F(M_{c1})$ estimated from M_{c1} became larger than ξ with decreasing cross-link densities in any case.

The triangular symbols R_F(sol) in Figure 7b were calculated by substituting the average molecular weight between "chemical" cross-link sites in eq 9. This quantity could be determined from the measurements of sol fraction in cross-linked samples by assuming the gelation theory, which was proposed by Gottlieb et al.[11] The values of R_F(sol) were larger than any other R_F over the whole range of cross-link densities. In addition, the fraction of trapped entanglements estimated from the above gelation theory increased with cross-link densities.[42] It follows that trapped entanglements in swollen networks may be almost equivalent to chemical cross-link sites at the equilibrium state of swelling. In other words, the mesh size of swollen networks estimated from the application of the C^* theorem or from DLS measurements implies an average distance between two "junctions" in swollen networks, which contain both physical (trapped entanglements) and chemical cross-link sites.[43] The above discussion is also fundamentally the case for the FR equation, though the absolute value of M_{c1} differs from that of M_{c2}.[5,15] However, it is unknown whether or not "all" trapped entanglements in real swollen networks act as physical cross-link sites. Nevertheless, trapped entanglements appear to be somewhat present in end-linked networks PDMS, compared with DCP-cured NR.[10,42]

Consequently, it has become apparent experimentally that ξ represents the mesh size in swollen networks and that M_{c2} may be valid. On the contrary, M_{c1} seems to be at least overestimated at (much) lower cross-link densities. This is believed to be due to nonaffine behavior of an individual network chain.[14] Perhaps, as suggested from SANS experiments, an unfolding of the network chain and/or a rearrangement of a cross-link site may occur primarily rather than an extension (or deformation) of each network chain in the course of swelling.[13,14,20] If so, it is at least necessary to thermodynamically reconsider the conventional concept of swelling mechanism in the FR equation, especially the variations of elastic free energy during swelling, which have so far been derived from the classical theory of rubberlike elasticity. Geissler et al.[44] have been attempting to quantitatively study the above problem. At present the strain function in the FR equation has been modified on the basis of the "constrained-junction model".[8] However, even in the above model, it is difficult to explain the variations of R_F in swollen cross-linked polymers measured by SANS experiments.[14] Determining unequivocally the parameters κ and ζ of the strain function in the modified FR equation is quite cumbersome in the case of swollen rubber vulcanizates,[14] and this equation cannot be used as a "routine" method for the characterization of network structure.[14,45] In addition, there still remains the question of additivity of Gibbs' free energies.[14,45]

Here, it should be noted that the C^* theorem suggests intuitionally and automatically the analogy between semidilute polymer solutions and swollen cross-linked polymers and that this theorem does not entirely refer to the swelling mechanism itself.[16] Nevertheless, the M_c dependence on C_e in the C^* theorem is qualitatively similar to that in the FR equation under a low-concentration approximation,[15] and if one may assume that the so-called memory term in the FR equation varies with M_c to the power of −0.5, the above relation in the FR equation is the same power law as that in the C^* theorem, except for the numerical coefficient.[20]

Swelling behaviors of rubber vulcanizates at or near the Θ-state conditions is very interesting for the purpose of investigating the unfolding of network chains and/or the rearrangements of cross-link sites in the process of swelling of a cross-linked rubber with (much) lower cross-link densities.[40] In the near future, the DLS for rubber vulcanizates swollen in a poor solvent will be measured.

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