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Uniaxial elongation of deswollen polydimethylsiloxane networks with supercoiled structure

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The mechanical properties of polydimethylsiloxane networks with a supercoiled structure, which are prepared by removing solvent from the networks crosslinked at low concentration, have been investigated. The fractal dimension D of the supercoiled structure has been estimated to be $D = 2.5$ from the dependence of stress on the elongation ratio λ on the basis of the concept of the Pincus blob. The obtained D is larger than for Gaussian chains ($D = 2$), and smaller than for 'polymer chain in an array of obstacles' (PCAO) models ($D = 3$ or 4). The deswollen network prepared at *ca* 9% has exhibited a remarkable high extensibility reaching $\lambda \cong 18$, as a result of the reduction of the distance between network junctions on deswelling and the decrease of trapped entanglements due to the low concentration at crosslinking. From comparison of the stress–elongation relationships in the deswollen and preparation state, the deswollen networks with a supercoiled structure after a large elongation are expected to have the same topological structure for the network chains as the original networks under elongation.

(Keywords: supercoiling; deswelling; high extensibility)

INTRODUCTION

The elastic properties of deswollen polymer networks, which are prepared by removing solvent from the network crosslinked in solution, are still an unsolved problem in the physics of rubber elasticity[1–3]. The deswelling process is accompanied by the collapse of network chains due to the volume decrease of material, which complicates the quantitative understanding of the elasticity of deswollen networks. The contraction of polymeric network chains on deswelling has often been called *supercoiling*[1–4]. The supercoiled chains are expected to have a contracted conformation compared with Gaussian chains. In fact, recent neutron scattering experiments showed[5,6] that the gyration radius of the network chains in the fully deswollen state is smaller than the unperturbed dimension. However, details of the conformation of supercoiled chains, and the effects of supercoiling on the mechanical properties of deswollen networks have not been elucidated.

Recently, the topological structure of the collapsed polymer systems, which is represented by the deswollen network, has attracted attention[7–11]. Several authors[7–11] have discussed the applicability of 'the polymer chain in an array of obstacles' (PCAO) model[7–14] to the collapsed polymer systems. The PCAO is modelled by a random walk on the lattice with the obstacles corresponding to the topological constraints. The fractal dimension (D) of the PCAO model for a closed random walk (a ring chain) is reported[7–14] to be $D = 3$ or 4 depending on whether it is with or without the excluded volume effect, respectively. The PCAO model has a strongly collapsed conformation compared with the Gaussian chain ($D = 2$). Obukhov *et al.*[7] have applied the PCAO model to the supercoiled structure, and predicted that the deswollen networks with supercoiled structure have a rather different stress–elongation relationship compared with the network composed of Gaussian chains. They have also pointed out[7] the possibility of high extensibility for deswollen networks prepared at low concentration, which originates from the reduction of end-to-end distance of entangled chains on deswelling and the decrease of trapped entanglements by lowering the preparation concentration.

Experiments on the elasticity of deswollen networks have been reported by several researchers[4,15–17]. Vasiliev *et al.*[4] indicated that the concentration dependence of the elastic modulus of deswollen networks prepared at low concentrations is quite different to the predictions of classical rubber elasticity theory. According to their results, a considerable degree of supercoiling occurs for the networks prepared at low concentration, and with network chains having a relatively large polymerization index (N). In the other studies[15–17], the effect of supercoiling on the elasticity was not observed clearly, which is a result of experimental conditions where the magnitude of supercoiling was small: the preparation concentrations were not so low, and/or N of the network chain was small.

The complicated concentration dependence of elastic modulus of deswollen networks, which implies the formation of supercoiled structure, has been reported[4], but the stress–elongation relationship of the deswollen networks with the supercoiled structure, which includes important information about the topological structure of networks, has not been investigated experimentally. In

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this study, we have prepared the network by the end-linking procedure with the prepolymer having a relatively large N over a wide concentration range. The preparation concentration dependence of the elastic modulus and the stress–elongation relation of the deswollen networks has been investigated. The effects of supercoiling on elastic modulus and stress–elongation behaviour have been demonstrated by comparing the mechanical properties of the networks in the preparation and the deswollen state. (We call the network in the preparation state the *original network*.) The stress–elongation behaviour of the deswollen network with the supercoiled structure has been analysed on the basis of treatment of a large deformation for a flexible polymer chain by Pincus[18]. The fractal dimension of supercoiled structure has been evaluated from the stress dependence on the elongation ratio in the large deformation region. We have also shown that the deswollen network prepared at low concentration exhibits a remarkable high extensibility.

EXPERIMENTAL

The networks were prepared by hydrosilylation in toluene between the vinyl-terminated polydimethylsiloxane (PDMS) (Chisso Co., Japan) and tetrakis(dimethyl siloxy)silane (TDMS) (Chisso Co., Japan). The molecular weight of PDMS is $M_w = 4.7 \times 10^4$, which was determined by light scattering, and the value of M_w/M_n is 1.6, which was measured by g.p.c. Here, M_w and M_n are the weight and the number average molecular weight, respectively. $H_2PtCl \cdot 6H_2O$ dissolved in 2-propanol (Spier's catalyst) was used as a catalyst for hydrosilylation[19,20]. The crosslinking was carried out for solutions with eight kinds of polymer volume fraction (ϕ_o') with the optimum value of r (the ratio of silane hydrogens to vinyl groups) (r_{opt}). The value of r_{opt} at each ϕ_o' was determined from the minimum in the r dependence of the degree of equilibrium swelling at each ϕ_o'. The sample prepared at $r = r_{opt}$ was regarded as the network having as small a number of structural defects as possible[21,22]. The details of this method are described in ref. 21 and our previous paper[22]. The procedure of sample preparation was as follows. The solutions were cast in a Teflon mould. The sealed mould was kept at 100°C for 24 h for the hydrosilylation reaction. For the sample with $\phi_o' = 0.0985$, the cure for 24 h was insufficient for the complete reaction, and this sample was cured for 3 days. After the sample was removed from the mould, a part of the sample was used for mechanical measurements as the original network sample. The rest of the sample was divided into two parts. One was kept in air to obtain the fully deswollen network for mechanical measurements. The complete drying required several days. The effect of drying rate on the structure of deswollen networks will be described later. The other part was used for the measurement of the weight fraction of the soluble species. In order to wash out the unreacted species, it was immersed in toluene until equilibrium swelling was achieved. Then, the swollen sample was completely dried in air. The weight of the dry sample was measured, and then the weight fraction of soluble species was calculated. The polymer volume fraction of the network in preparation state (ϕ_o) was re-calculated by subtracting the unreacted portion from ϕ_o'. The fraction of soluble species was less than 8 wt% for samples with $\phi_o' \geqslant 0.191$. For the sample with $\phi_o' = 0.0985$, the sol fraction was 12.1 wt%, which was somewhat larger than those for other samples. This would be due to the difficulties involved in hydrosilylation at the very low polymer concentration.

The drying rate of the samples possibly influences the structure of the dry networks. In order to check the effect of deswelling methods on the structure of dry networks, we prepared a dry network with $\phi_o' = 0.191$ by removing solvent as slowly as possible: the composition of solvent for deswelling was changed gradually, i.e. the ratio of methanol to toluene was gradually stepped up from 0 to 100% with steps of 20%. The achievement of equilibrium swelling at each stage was checked through weighing of samples. The size of deswollen sample in 100% methanol was comparable to that of dry sample. Finally, methanol was vaporized in air to obtain the dry network. The dry network sample prepared by the slow deswelling process showed the same stress–elongation behaviour and elastic modulus as that prepared by drying the sample in the preparation state in air. This result suggests that the two deswelling methods are regarded as the quasi-static process. We did not employ the slow deswelling process described above as the standard deswelling method in this study, because the process requires a long period, i.e. several months.

The stress–elongation relation and the initial Young's modulus in preparation and dry state (E_i and E_d, respectively) of the samples were measured by uniaxial elongation at room temperature. The initial length of samples was *ca* 20 mm, and the elongation was carried out at the constant crosshead speed (v) of 10 mm min^{-1}. This condition satisfied the quasi-equilibrium condition, which was confirmed by the fact that the stress–elongation relation of each sample was independent of v in the region of $v \leqslant 20$ mm min^{-1}. The effect of the unreacted species in the samples on the elastic behaviour was eliminated, because the unreacted species do not contribute the elastic behaviour of the networks under the equilibrium condition. The elongational measurement of the original network with $\phi_o = 0.0877$ could not be performed due to the softness of material. The values of ϕ_o, r_{opt}, E_i and E_d at each ϕ_o' are given in *Table 1*.

RESULTS AND DISCUSSION

Effect of supercoiling on elastic modulus of deswollen networks

In our previous paper[22], it was shown that the ϕ_o dependence of the elastic modulus of the original and the

Table 1 Polymer volume fraction of the solution for preparation (ϕ_o'), polymer volume fraction and initial Young's modulus of the network in preparation state (ϕ_o and E_i, respectively) and initial Young's modulus of the fully deswollen network (E_d) and the optimal ratio of silane hydrogen to vinyl group (r_{opt})

ϕ_o'	ϕ_o	r_{opt}	$10^{-4}E_i$ (Pa)	$10^{-4}E_d$ (Pa)
1.00	1.00	1.15	34	34
0.861	0.852	1.20	28	30
0.725	0.709	1.14	19	22
0.564	0.544	1.07	8.9	16
0.430	0.411	1.24	5.8	14
0.298	0.281	1.18	2.6	10
0.191	0.179	1.20	0.89[a]	6.9
0.0985	0.0877	1.10	–	3.3

[a] The value of E_i for the samples with $\phi_o \geqslant 0.179$ has been reproduced from ref. 22

fully swollen networks is interpreted in terms of the model proposed by Panyukhov[23] together with our considerations for the effects of trapped entanglements and the concentration regime of preparation state on the elasticity. The model is based on the assumption of the affine displacement of crosslinking points relative to the global network. Here, we attempt to interpret the ϕ_o dependence of the elastic modulus of the fully deswollen networks by means of this model. The expression of the elastic modulus (E) of the network with the polymer volume fraction ϕ, which is prepared at ϕ_o, is given as follows[7,22,23].

$$E(\phi_o, \phi) \cong \frac{k_B T}{a^3} \frac{\phi}{N_e(\phi_o)} \lambda_s^2 \alpha_T^2 \qquad (1)$$

where k_B is the Boltzmann constant, and T is the absolute temperature, and a^3 is the volume occupied by the monomer, and $N_e(\phi_o)$ is the length in polymerization index between the neighbouring junctions at ϕ_o regardless of whether these are trapped entanglements or chemical crosslinks, λ_s is the swelling coefficient defined as $\lambda_s = (\phi/\phi_o)^{-1/3}$, and α_T is the expansion coefficient defined as $\alpha_T = R_o/R$. Here, R_o is the root of mean square end-to-end distance of the connected prepolymer chain at ϕ_o, and R is the end-to-end distance of the prepolymer chain in the unconnected state in the solution at ϕ. According to scaling theory[2], R scales as $R \sim \phi^{(2\nu-1)/(2-6\nu)}$ in semidilute regime where ν is the excluded volume exponent, while R in concentrated regime is equal to the unperturbed dimension corresponding to $\nu = 1/2$. Equation (1) with $\phi = \phi_o$ gives the description of $E_i (= E(\phi_o, \phi_o))$ as $E_i \cong a^{-3} k_B T \phi_o N_e(\phi_o)^{-1}$. The expression of $E_d (= E(\phi_o, 1))$ is obtained from equation (1) with $\phi = 1$ as $E_d \cong a^{-3} k_B T \phi_o^{1/(9\nu-3)} N_e(\phi_o)^{-1}$ in which $\nu = 0.57$ in the region $\phi_o < \phi_o^{**}$ and $\nu = 1/2$ in $\phi_o > \phi_o^{**}$ is employed[22], respectively. Here, ϕ_o^{**} is the value of ϕ_o at the boundary in respect to R_o between the semidilute and the concentrated regime, and $\nu = 0.57$ is obtained from the relationship between the molecular weight (M) and the intrinsic viscosity ($[\eta]$) for PDMS in toluene[24], namely, $[\eta] \sim M^{3\nu-1}$. The relation between E_i and E_d is obtained as follows.

$$E_d \cong \phi_o^{(-9\nu+4)/(9\nu-3)} E_i \qquad (2)$$

Figure 1 shows the plots of $E_d \phi_o^{(9\nu-4)/(9\nu-3)}/E_i$ against ϕ_o. Here, we used $\nu = 0.57$ for the samples prepared at the region $\phi_o < 0.6$, and $\nu = 1/2$ for those at $\phi_o > 0.6$. The value of ϕ_o^{**} was regarded as $\phi_o^{**} \cong 0.60$, which was reported by Adachi *et al.*[25]. The validity of this treatment for ϕ_o^{**} was discussed in previous paper[22]. It is seen in *Figure 1* that the quantity, $E_d \phi_o^{(9\nu-4)/(9\nu-3)}/E_i$, is almost equal to unity in $\phi_o > 0.7$, while it is larger than unity in the region $\phi_o < 0.7$ and the deviation from unity becomes larger as ϕ_o decreases. The model considers the changes of the two physical quantities accompanying the deswelling for the evaluation of elastic modulus: the number density of the elastic effective chains and the end-to-end distance of the network chains. The change of the end-to-end distance of network chains is estimated on the basis of the consideration for the Gaussian or excluded volume chain. The end-to-end distance of network chains at deswollen state should be smaller as the volume decrease

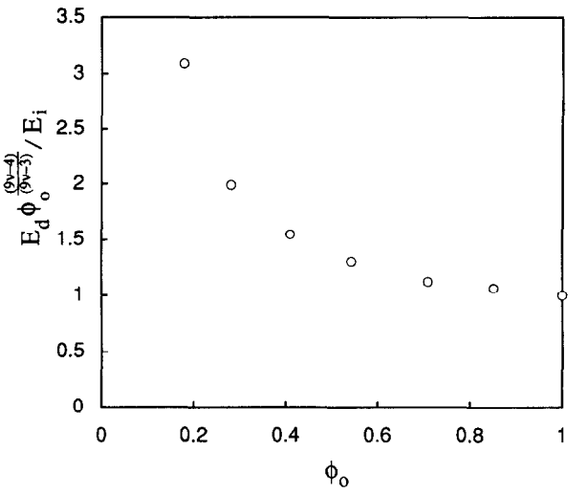

Figure 1 Plots of $E_d \phi_o^{(9\nu-4)/(9\nu-3)}/E_i$ against ϕ_o. $\nu = 0.57$ and $1/2$ are used for the samples prepared at $\phi_o < 0.6$ and $\phi_o > 0.6$, respectively

on deswelling is larger. In low ϕ_o region where the volume decrease of network accompanying the deswelling is large ($\lambda_s < 1$), the conformation of network chains in dry state deviates largely from the Gaussian conformation. The phase space around the network chains is expected to decrease due to the contracted conformation of supercoiled chains, which leads to the higher elastic modulus than that predicted by the theory for the Gaussian or excluded volume chain. This effect of supercoiling on the elastic modulus is recognized by experimental values higher than unity in the low ϕ_o region in *Figure 1*.

On the other hand, it is seen in *Figure 1* that equation (1) succeeds in the description of experimental results in the high ϕ_o region. In high ϕ_o region, the magnitude of supercoiling of network chains is small, because the volume change accompanying the deswelling is small, namely, $\lambda_s \cong 1$.

The quantities ϕ and ϕ_o in the theory do not include the portion of the dangling chains not contributing to the elasticity. We observed (unpublished data) that the dynamic Young's modulus (E') of the original network at each ϕ_o is almost constant over the wide range of the frequency (ω) ($0.01 \leqslant \omega \leqslant 100\,s^{-1}$). This result suggests that the amount of the dangling chain is negligible for the network samples in this study. Patel *et al.*[21] reported that the end-linked PDMS networks having a considerable amount of dangling chains showed a noticeable dependence of E' on ω. We use ϕ_o without taking the portion of the dangling chains into account in the later calculation.

Effect of supercoiling on stress–elongation behaviour of deswollen networks

In *Figure 2* we show the double logarithmic plots of reduced stress against elongation ratio for the original networks. The stress (σ_e) is the engineering stress defined by the force divided by the cross-sectional area in undeformed state. The elongation ratio (λ) is defined by $\lambda = l/l_o$, where l_o and l is the length of sample in undeformed and deformed state, respectively. The stress in *Figure 2* is renormalized by E_i of each sample. The dashed curve corresponds to the stress–elongation relation for Gaussian network[26] expressed as $\sigma_e/E_i = (\lambda - \lambda^{-2})/3$. It is seen that the experimental

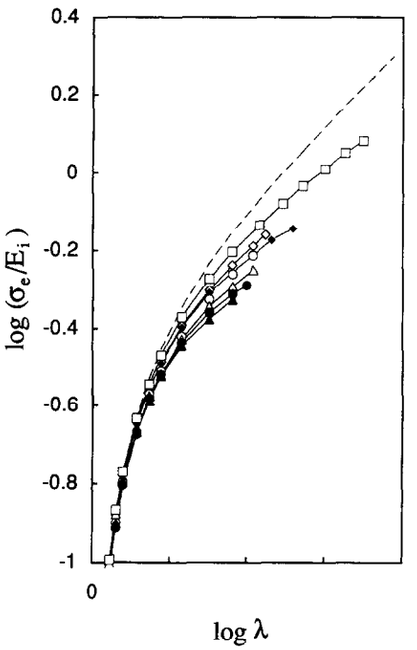

Figure 2 Double-logarithmic plots of σ_e/E_i against λ for the original networks. (▲) 1; (●) 0.852; (△) 0.709; (○) 0.544; (◆) 0.411; (◇) 0.281; (□) 0.179 where each value corresponds to ϕ_o. The dashed curve represents the stress–elongation relation for the Gaussian network

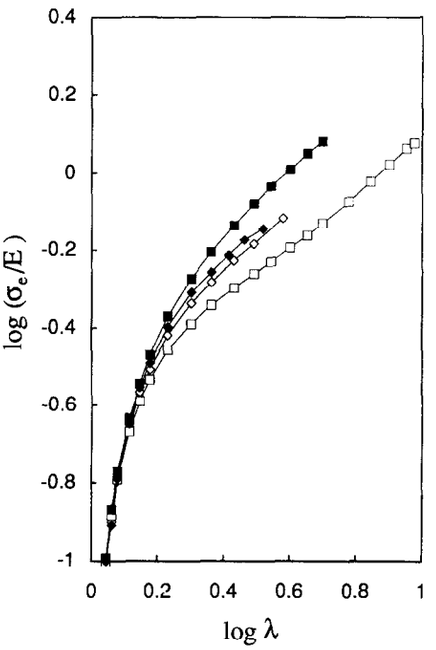

Figure 4 Comparison of the reduced stress–elongation relations of the original and the dry networks. The stress for the original and the dry network is reduced by E_i and E_d, respectively. (□) Dry network with $\phi_o = 0.179$; (■) original network with $\phi_o = 0.179$; (◇) dry network with $\phi_o = 0.411$; (◆) original network with $\phi_o = 0.411$

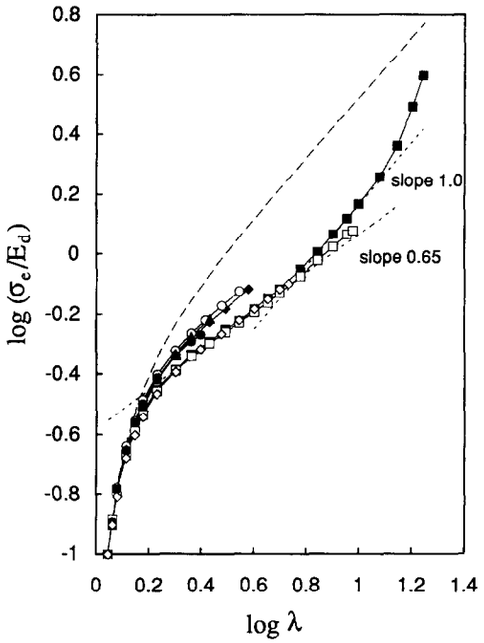

Figure 3 Double-logarithmic plots of σ_e/E_d against λ for the fully deswollen networks. (■) is the data for $\phi_o = 0.0877$. The other symbols are the same as in *Figure 2*. The dashed curve represents the stress–elongation relation for the Gaussian network

curves are described by the dashed curve in small λ region, while those deviate downwards from the dashed curve as λ increases. This is the well known result for the stress–elongation behaviour of the usual elastomers[1,3,26]. Qualitatively, the downward deviation is interpreted similarly as the C_2 term in the Mooney–Rivlin equation[1,3,26]. The major factor for the downward deviation has often been attributed to the effect of entanglements[1,3,26]. The number of trapped entanglements decreases as ϕ_o is lowered. It can be seen in *Figure 2* that as the network is prepared at lower concentration, the degree of deviation from the dashed curve is smaller, which supports the above consideration qualitatively. The decrease of ϕ_o, i.e. the decrease of the number of trapped entanglements also leads to the increase of the extensibility as seen in *Figure 2*.

We indicate the stress–elongation relations for the deswollen networks in *Figure 3*. The stress is renormalized by E_d of each sample. It is found that the stress–elongation relations of deswollen networks are classified into two groups: the networks prepared at $\phi_o \leqslant 0.281$, and those at $\phi_o \geqslant 0.411$. The overlapping of the curves suggests that the deswollen networks in each group have common topological features. The major difference of curves in each group is only in the extensibility. The dependence of σ_e on λ for the deswollen networks with $\phi_o \leqslant 0.281$ is found to obey $\sigma_e \sim \lambda^{0.65}$ in the region $2.1 \leqslant \lambda \leqslant 5.5$. It is also seen that the deswollen network prepared at $\phi_o = 0.0877$ shows the high extensibility reaching $\lambda \cong 18$. The detailed analysis of the dependence of σ_e on λ and the extensibility will be discussed later.

In *Figure 4* we show the comparison of the stress–elongation relation in the deswollen and the preparation state for $\phi_o = 0.411$ and $\phi_o = 0.179$. The stress for the deswollen and the original network is reduced by E_d and E_i, respectively. The dry network prepared at $\phi_o = 0.411$ is found to show almost the same stress–elongation relation as the original network. For all other samples prepared at $\phi_o \geqslant 0.411$, the curves for dry and preparation state almost overlap each other (and the data are not shown in the figure), suggesting that the deswelling does not have a great influence on the stress–elongation behaviour for the networks prepared at $\phi_o \geqslant 0.411$, and the topological structure of the networks does not change greatly on deswelling. The effect of supercoiling

on E_d is also relatively small in the region $\phi_o \geqslant 0.411$ as seen in *Figure 1*.

On the other hand, the stress–elongation behaviour of dry network prepared at $\phi_o = 0.179$ deviates greatly from that of the Gaussian network as indicated in *Figure 3*, and is rather different from that of the original network as shown in *Figure 4*. A similar result is obtained for the sample with $\phi_o = 0.281$. The large difference in the stress–elongation behaviour between the dry and the original network in the region $\phi_o \leqslant 0.281$ should be due to the supercoiled structure formed on deswelling, the details of which will be described later. The stress–elongation relations of deswollen networks with supercoiled structure have a weaker dependence of σ_e on λ in the region $\lambda \leqslant 5.5$ compared with that of the original networks. The stress–elongation relation in $\lambda \leqslant 5.5$ is independent of ϕ_o, and the relation $\sigma_e \sim \lambda^{0.65}$ in $2.1 \leqslant \lambda \leqslant 5.5$ is common to the stress–elongation behaviour for the dry networks with supercoiled structure. In the region $\phi_o \leqslant 0.281$, the effect of supercoiling on the Young's modulus is also large as seen in *Figure 1*.

The clear classification of the stress–elongation relations into two groups appears to suggest that the supercoiling of the network chains occurs abruptly at a critical value of ϕ_o, which is located at $0.281 \leqslant \phi_o \leqslant 0.411$. On the other hand, the effect of supercoiling on the elastic modulus appears in the region $\phi_o \leqslant 0.54$, and increases gradually as ϕ_o decreases, as seen in *Figure 1*. The elastic modulus may be more sensitive to the supercoiling of network chains than the stress–elongation relationship. However, the overlapping of the stress–elongation curves in the low ϕ_o region strongly suggests that the supercoiled structure settles into the steady one specific to the system in this study as ϕ_o decreases. We estimate the fractal dimension (D) of the (steady) supercoiled structure from the dependence of σ_e on λ under the disentanglement process of the supercoiled structure as shown below.

Analysis of disentanglement process of supercoiled structure

We analyse here the stress–elongation behaviour of the deswollen networks on the basis of the treatment of the large deformation for a flexible polymer chain by Pincus[18]. According to this treatment, the strongly stretched polymer chain is regarded as a nearly linear sequence of the smaller units (Pincus blobs) with size ξ_p. The features of a Pincus blob are summarized as follows[2,7,18,27]: inside a Pincus blob (the distance $r < \xi_p$), the applied force (f) is a weak perturbation, while f is a strong perturbation at the scale $r > \xi_p$. This condition postulates the relation $f\xi_p \cong k_B T$; the correlation inside a Pincus blob ($r < \xi_p$) is the same as for the global chain. This means that the structure of the global chain is preserved inside the Pincus blob during the elongation process as long as the network structure concerned is not completely disentangled by elongation, and the blob size is given by $\xi_p \cong a' g_p^{1/D}$ where a' is the unit length, and g_p is the number of monomers in Pincus blob, and D is the fractal dimension of the polymer chain. Assuming affine deformation on a scale larger than the size of the polymer chain, the following relation between λ and f is obtained.

$$\lambda \cong \frac{(N/g_p)\xi_p}{R^o} \cong \frac{Na'}{R^o}\left(\frac{a'f}{k_B T}\right)^{D-1} \tag{3}$$

where R^o is the end-to-end distance of the polymer chain in the undeformed state. The global stress for the network composed of the polymer chains above, σ_e, is related to f through $\sigma_e \cong \mu R^o f$ where μ is the number density of the effective elastic chains. We get the following relation between σ_e and λ.

$$\sigma_e \sim \lambda^{1/(D-1)} \tag{4}$$

It can be seen in *Figure 3* that the dependence of σ_e on λ for the deswollen networks with supercoiled structure obeys $\sigma_e \sim \lambda^{0.65}$ in the region $2.1 \leqslant \lambda \leqslant 5.5$. Considering the region $2.1 \leqslant \lambda \leqslant 5.5$ as the disentanglement process of the supercoiled structure, we evaluate the fractal dimension for the supercoiled structure to be $D = 2.5$ from equation (4). This fractal dimension ($D = 2.5$) is larger than $D = 2$ for the Gaussian chain, while it is smaller than $D = 3$ or 4 for PCAO model. The exponent of the dependence of σ_e on $\lambda(\sigma_e \sim \lambda^p)$ is $p = 1$ for the Gaussian network, and $p = 1/2$ and $1/3$ for PCAO model with $D = 3$ and 4, respectively. Obukhov *et al.*[7] predicted $\sigma_e \sim \lambda^{1/3}$ by applying the PCAO model with $D = 4$ to the supercoiled structure. Our experimental result suggests that the present supercoiled chain is more contracted than the Gaussian one, while it is not collapsed as strongly as the PCAO models. The reason for the smaller D in this study compared with those of the PCAO model might be that the PCAO model requires a very long network chain: N/N_e in the PCAO model is so large that the distance between the neighbouring obstacles is regarded[7,14] as $bN_e^{1/2}$. The value of $N/N_e(1)$ in this study is estimated to be *ca* 6 using $M_e \cong 8100$ for PDMS[28] where M_e is the molecular weight between the neighbouring entangled points in melt in the uncrosslinked state. Furthermore, the value of N/N_e for the networks prepared at low ϕ_o becomes much smaller, because N_e increases as ϕ_o decreases. From the viewpoint of N/N_e, the experimental condition in this study may not match sufficiently with the situation where the PCAO model is applicable.

Analysis of the whole elongation process of the deswollen networks with supercoiled structure

We clarify here the changes in the topological structure of the supercoiled chains during the whole elongation process by comparing the stress–elongation behaviour in the deswollen and the preparation state. Here, we assume that the crosslinking points moves affinely relative to the global network on deswelling and elongation. We define the reduced elongation ratio for the deswollen network (λ_p) by regarding the undeformed state of original network as the reference state for the elongation as follows.

$$\lambda_p = \phi_o^{1/3}\lambda \tag{5}$$

Figure 5 indicates the stress–elongation relation for the deswollen network with $\phi_o = 0.179$, where λ_p is employed as the elongation ratio ($\lambda_p \cong 0.56\lambda$). The stress–elongation relation for the original network with $\phi_o = 0.179$ is also shown in the figure ($\lambda_p = \lambda$). The stress in the figure for the deswollen and original network is reduced by E_d and E_i, respectively. It is seen that the disentanglement process of the supercoiled structure begins at $\lambda_p \cong 1.2$, meaning that the disentanglement of supercoiled chains starts when the end-to-end distance

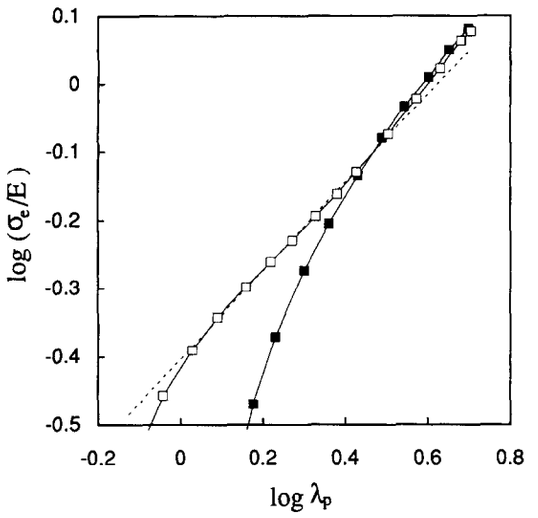

Figure 5 Comparison for the reduced stress–elongation relations of the network with $\phi_0 = 0.179$ at the preparation and the dry state. λ_p is the reduced elongation ratio given by equation (6). (□) Dry state; (■) preparation state. The dashed straight line has a slope of 0.65

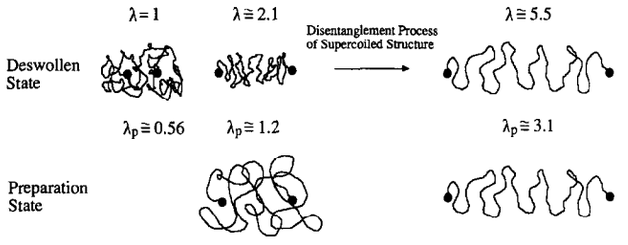

Figure 6 Schematic representation for the whole elongation process of deswollen networks with supercoiled structure at $\phi_0 = 0.179$. The corresponding state of the original network is also shown

of network chains reaches a distance slightly larger than R_0. The disentanglement process of the supercoiled structure continues up to $\lambda_p \cong 3.1$, and then the dependence of σ_e on λ becomes stronger as $\lambda_p > 3.1$. The following two significant points should be noted for the comparison of the stress–elongation curves of the deswollen and the original network in *Figure 5*: both curves coincide at $\lambda_p \cong 3.1$ where the supercoiled structure has been completely disentangled; both curves almost overlap each other in the region $\lambda_p \geqslant 3.1$, i.e. after the complete disentanglement of the supercoiled structure. These results suggest that the topological structure of the network chains of the deswollen gel just at the end of the disentanglement process of supercoiled structure is similar to that of the original network elongated to $\lambda = 3.1$. In *Figure 6* we show the schematic representation for the whole elongation process of the deswollen network with supercoiled structure and the corresponding states of the original network.

It should be noted that the stress–elongation behaviour of the dry network prepared at $\phi_0 = 0.0877$ has various interesting features. It can be seen in *Figure 3* that the dependence of σ_e on λ obeys $\sigma_e \sim \lambda^{0.65}$ in the region $2.1 \leqslant \lambda \leqslant 5.5$ similar to $\phi_0 = 0.179$, while in the region $7 \leqslant \lambda \leqslant 12$ where the supercoiled structure is completely disentangled, the relation is expressed as $\sigma_e \sim \lambda^{1.0}$ corresponding to that for a Gaussian network in the large deformation region. The region $5.5 \leqslant \lambda \leqslant 7$ is the marginal regime where the dependence of σ_e on λ changes from $\lambda^{0.65}$ to $\lambda^{1.0}$. The linear relation between σ_e and λ in the region $7 \leqslant \lambda \leqslant 12$ suggests that the topological structure of the network chains where the supercoiled structure is completely disentangled is similar to that of the Gaussian chain. In *Figure 2* we showed that the stress–elongation behaviour in the preparation state is closer to the Gaussian one as ϕ_0 decreases. The stress–elongation behaviour of the original network with $\phi_0 = 0.0877$ is expected to be closer to the Gaussian one than that with $\phi_0 = 0.179$, though it was not measured due to the softness of the material. If the stress–elongation behaviour of the original network with $\phi_0 = 0.0877$ is assumed to be Gaussian, the whole elongation process of dry network with $\phi_0 = 0.0877$ is interpreted in the manner indicated in *Figure 6*.

The crossover of the dependence of σ_e on λ from the specific behaviour of the structure concerned with the Gaussian behaviour has been predicted theoretically by several authors[7,18]. However, the crossover was not reported experimentally, which is due to the fact that the usual polymer networks do not possess sufficiently high extensibility to bear the large elongation reaching the crossover region. The perfect crossover to the Gaussian behaviour may occur for networks with high extensibility and few trapped entanglements, because the dependence of σ_e on λ in the high λ region for $\phi_0 = 0.179$ obeys $\sigma_e \sim \lambda^{0.77}$, while the perfect crossover to the Gaussian behaviour is observed for $\phi_0 = 0.0877$. The exponent smaller than unity for $\phi_0 = 0.179$ might result from the effect of trapped entanglements. Actually, the stress–elongation behaviour of the original network with $\phi_0 = 0.179$ does not agree perfectly with the Gaussian one due to the effect of trapped entanglements, as seen in *Figure 2*. The perfect crossover to the Gaussian behaviour for $\phi_0 = 0.0877$ would be due to no or a negligible amount of trapped entanglements in the network. The estimation of the amount of trapped entanglements for the network with $\phi_0 = 0.0877$ will be shown later.

In *Figure 3* the stress–elongation curve of the dry network with $\phi_p = 0.0877$ is found to indicate the upturn in the region $\lambda > 12$. The strong dependence of σ_e on λ in the region $\lambda > 12$ is due to the deviation of the network structure from the Gaussian one by the large elongation. The large elongation leads to the approach to the full extension of network chains. It is well known[26] for the stress–elongation behaviour of the crosslinked rubbers that the approach to the full extension of network chains results in a strong dependence of σ_e on λ.

High extensibility of the deswollen network prepared at low concentration

The deswollen network prepared at $\phi_0 = 0.0877$ exhibits a remarkable high extensibility, reaching $\lambda \cong 18$ (*Figure 3*). (Perfect size recovery has been observed for the deswollen network with $\phi_0 = 0.0877$ elongated up to $\lambda \cong 15$.) The possibility of high extensibility for deswollen networks prepared at low ϕ_0 has been pointed out theoretically by Obukhov *et al.*[7]. The high extensibility results from two main factors: the reduction of the distance between the neighbouring junctions on deswelling; the decrease of the amount of

trapped entanglement, which is an origin of failure, due to the low ϕ_o. It is qualitatively confirmed in *Figure 3* that the extensibility of deswollen networks increases as ϕ_o decreases. According to their simple evaluation for the extensibility of polymer network[7], the theoretical limit of extensibility (λ_{max}) for the deswollen network prepared at ϕ_o is estimated as follows.

$$\lambda_{max} \cong \frac{aN_e(\phi_0)}{aN_e^{1/2}(\phi_0)\phi_o^{1/3}} = \frac{N_e^{1/2}(\phi_0)}{\phi_o^{1/3}} \quad (6)$$

The quantity $N_e(\phi_o)$ for the system in this study was obtained as $N_e(\phi_o) \cong N_e(1)\phi_o^{-1.1}$ from the ϕ_o dependence of E_i in the region $\phi_o \geqslant 0.179$ in our previous study[22]. The value of $N_e(1)$ is estimated to be *ca* 13 Kuhn segments from $M_e = 8100$[28] and the number of real bonds per free joint link for PDMS $\cong 17$[29]. If $N_e(\phi_o) \cong N_e(1)\phi_o^{-1.1}$ is employed for the estimation of N_e at $\phi_o = 0.0877$, the calculated value of N_e is found to be much larger than N of the prepolymer. Here, N of the prepolymer with $M = 4.7 \times 10^4$ is estimated to be *ca* 75 Kuhn segments. This means that the number of trapped entanglements is negligible compared with that of chemical crosslinks for the network at $\phi_o = 0.0877$. Accordingly, we should use N of the prepolymer instead of N_e in equation (6) for the network with $\phi_o = 0.0877$. We get $\lambda_{max} \cong 20$ from equation (6) with $N \cong 75$. It is well known[30] that the failure phenomena is primarily governed by the defects of the sample, which complicates the quantitative comparison of experimental results with the theory. However, the experimental failure point for the dry network with $\phi_o = 0.0877$ ($\lambda \cong 18$) is close to the theoretical value. Here, we should mention that $\lambda \cong 18$ is the highest extensibility that we have observed for the samples with $\phi_o = 0.0877$, and that is not an average one.

CONCLUSIONS

The formation of supercoiled structure on deswelling of PDMS networks crosslinked in solution has been demonstrated by investigating the preparation concentration dependence of the elastic modulus and the stress–elongation behaviour of deswollen networks. The considerable effects of supercoiling of network chains on the mechanical properties of deswollen networks are apparent for networks prepared at low concentration at which the volume decrease is large on deswelling. The deswollen networks with supercoiled structure have a higher elastic modulus than expected from the theory for the Gaussian chain or excluded volume chain, and shows the stress–elongation relation with the region where the dependence of stress on the elongation is much weaker compared with that for the original network. On the other hand, the deswollen networks prepared at high concentration, whose volume does not change greatly on deswelling, show the elastic modulus explained by the theory, and similar stress–elongation behaviour to the original networks.

The fractal dimension of supercoiled structure has been estimated from the dependence of stress on the elongation ratio in terms of the concept of the Pincus blob. The dependence of stress on the elongation ratio under the disentanglement process of the supercoiled structure is independent of preparation concentration, and common to the deswollen networks with a supercoiled structure. The obtained fractal dimension is larger than that of the Gaussian chain, and smaller than those of the PCAO model. The supercoiled chain is expected to be contracted in comparison with the Gaussian one, and not collapsed as strongly as the PCAO models.

The reduced stress–elongation behaviour of the deswollen network, where the elongation ratio is reduced by the undeformed state of the original network, is similar to the stress–elongation relation of the original network after the supercoiled structure is completely disentangled. This suggests that after the complete disentanglement of supercoiled structure, the topological structure of the network chains of deswollen networks is identical with that of the elongation original network. For the deswollen network prepared at *ca* 9% which is supposed to have few trapped entanglements, the dependence of stress on elongation has been found to crossover from the specific behaviour of the supercoiled structure to that of the Gaussian network.

The deswollen networks with supercoiled structure prepared at low concentration have shown the remarkable high extensibility originating from the reduction of the distance between the network junctions and the decrease in the number of trapped entanglements. In particular, the extensibility of the deswollen network prepared at *ca* 9% has reached *ca* 1700%, which has been found to be close to the theoretical limit of extensibility for the sample.

REFERENCES

1 Graessley, W. W. *Adv. Polym. Sci.* 1974, **16**, 1
2 de Gennes, P.-G. 'Scaling Concepts in Polymer Physics', Cornell University Press, Ithaca, New York, 1979
3 Heinrich, G., Straube, E. and Helmis, G. *Adv. Polym. Sci.* 1988, **85**, 33
4 Vasiliev, V. G., Rogovina, L. Z. and Slonimsky, G. L. *Polymer* 1985, **26**, 1667
5 Bastide, J. in 'Physics of Finely Divided Matter', Proceedings of Physics, Vol. 5, Springer, Berlin, 1985
6 Picot, C. *Prog. Coll. Polym. Sci.* 1987, **75**, 83
7 Obukhov, S. P., Rubinstein, M. and Colby, R. H. *Macromolecules* 1994, **27**, 3191
8 Khokhlov, A. R. and Nechaev, S. K. *Phys. Lett.* 1985, **112A**, 156
9 Grosberg, A. Y. and Nechaev, S. K. *Macromolecules* 1991, **24**, 2789
10 Grosberg, A. Y. and Nechaev, S. K. *Adv. Polym. Sci.* 1993, **106**, 1
11 Grosberg, A. Y. *Macromolecules* 1993, **26**, 3200
12 Helfand, E. and Pearson, D. S. *J. Chem. Phys.* 1983, **79**, 2054
13 Rubinstein, M. *Phys. Rev. Lett.* 1986, **57**, 3023
14 Nechaev, S. K. and Khokhlov, A. R. *Phys. Lett. A* 1988, **126**, 431
15 Price, C., Allen, G. de Candia, F., Kirkham, M. C. and Subramaniam, A. *Polymer* 1970, **11**, 486
16 Johnson, R. M. and Mark, J. E. *Macromolecules* 1972 **5**, 41
17 Ong, C. S. M. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn* 1974, **12**, 1599
18 Pincus, P. *Macromolecules* 1976, **9**, 386
19 Speier, J. L. *Adv. Organomet. Chem.* 1979, **17**, 407
20 Kohjiya, S., Ono, A. and Yamashita, S. *Polym.-Plast. Technol. Eng.* 1991, **30**, 351
21 Patel, S. K., Malone, S., Cohen, C., Gillmor, J. R. and Colby, R. H. *Macromolecules* 1992, **25**, 5241
22 Urayama, K. and Kohjiya, S. *J. Chem. Phys.* 1996, **104**, 3352
23 Panyukhov, S. V. *Sov. Phys. JETP* 1990, **71**, 372
24 Haug, V. A. and Meyerhoff, G. *Macromol. Chem.* 1962, **53**, 91
25 Adachi, K., Imanishi, Y., Shinkado, T. and Kotaka, T. *Macromolecules* 1989, **22**, 2391

26 Treloar, L. R. G. 'The Physics of Rubber Elasticity', 3rd Edn, Clarendon Press, Oxford, 1975
27 Daoudi, S. *J. Phys.* (*Paris*) 1977, **38**, 1301
28 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd Edn, Wiley, New York, 1980
29 Brandup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', 2nd Edn, Wiley, New York, 1975
30 Nielsen, L. E. 'Mechanical Properties of Polymers and Composites', Marcel Dekker, New York, 1975