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Extensive stretch of polysiloxane network chains with random- and super-coiled conformations

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Abstract. The stress-elongation (λ) relations at large deformations for the polymer network chains with randomcoiled and supercoiled conformations are investigated using the polysiloxane networks with high elongations at break far over 10. Supercoil is the conformation of network chains in deswollen polymer networks which are made by removing solvent from the networks crosslinked in solutions at low polymer concentrations. The validity of the scaling concept of Pincus blob for the mechanical response of a polymer chain is experimentally confirmed for the network composed of randomcoiled chains. The analysis of the stress-λ relations for the deswollen networks comprised of supercoiled chains on the basis of the Pincus blob concept suggests that supercoil is a much more contracted conformation relative to randomcoil.

PACS. 81.40.Jj Elasticity and anelasticity, stress-strain relations – 82.70.Gg Gels and sols – 83.80.Dr Elastomeric polymers

1 Introduction

Strongly contracted polymer chains under various constraints have attracted attentions of many physicists as an interesting topological system [1–5]. Due to their specific topology, the static and dynamic properties for such systems are theoretically expected to be significantly different from those for usual systems without any constraints. *Supercoil* has been assumed as one of unusually collapsed conformations of polymer chains [1,6–9]. Supercoil is the conformation of network chains in deswollen networks which are prepared by removing solvent (what we call *deswelling*) from the networks crosslinked in solution. We treat here a network made by so-called end-linking reaction between the precursor polymeric chains having functional groups at both the ends, and the low molecular-weight species with multi-functional sites (so-called crosslinker) [10]. The glass transition temperatures of the precursor chains concerned here are so low that they are in rubbery (liquid) state at room temperature. The conformation of the network chains just at crosslinking is substantially the same as that of precursor chains prior to crosslinking. Therefore, the conformation of the network chains just at crosslinking is described by an already known conformation of polymer chain in melt and solution such as *randomcoil* (*i.e.*, the Gaussian chain) and the conformation of the chains with excluded volume effects. In deswelling, a certain degree of volume decrease of the network system occurs as a result of a loss of the solvent: for example, if the polymer volume fraction at crosslinking is 0.1, the degree of volume reduction of the network system reaches *ca.* 90% of the initial volume. Since the densities of polymer and solvent are comparable in general, the density of the network system is not much changed before and after deswelling. It is naturally expected that the formation of voids does not occur in deswelling, since the network is in rubbery state after deswelling. In order to maintain the almost constant density before and after deswelling without forming voids, the network chains in deswollen state are requested to have a more contracted conformation than that of randomcoil. This requisite gives rise to the concept of supercoil which is quite different from randomcoil.

The details of supercoil have been unknown, though a small angle neutron scattering study reported [11] that the gyration radius of the network chains in deswollen polystyrene networks is smaller than the one in unperturbed state. Obukhov *et al.* [9] has theoretically pointed out the possibility that the deswollen networks prepared at low polymer concentrations reveal remarkable high extensibilities due to a smaller number of trapped entanglements as well as a shorter end-to-end distance of supercoiled network chains, relative to usual elastomeric networks. In previous study [12], we experimentally demonstrated their conception using poly(dimethylsiloxane) (PDMS) networks, and showed that the deswollen network prepared at *ca.* 10 wt% exhibited a high value of elongation ratio at break (λ_{max}) reaching *ca.* 20. We tried to estimate the fractal dimension of the supercoiled conformation from the analysis of the stress-elongation relation based on the scaling concept of the Pincus blob [12,13]. This concept predicts the following simple scaling law for

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the elongation ratio (λ) dependence of the stress (σ_e) at large deformations for a polymer chain with a structure characterized by fractal dimension D [13]:

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

where σ_e is the engineering stress defined as the force per cross-sectional area in undeformed state. Equation (1) has been employed in many theoretical studies on physical properties of polymeric systems [1,9,13–17], since the Pincus blob concept is widely applicable due to its physical significance as well as its simple form. However, it should be noted that the validity of equation (1) has not yet been fully confirmed in experiments. An experimental test for equation (1) is the measurement of the $\sigma_e - \lambda$ relation at large deformations for a polymer network composed of the network chains with an already known D. In this method, the network samples should satisfy the following two conditions: The first is that there are not any interactions between the network chains such as the entanglement coupling between different network chains which is termed trapped entanglement. This necessity arises from the fact that equation (1) originally concerns a single polymer chain. The second is that the extensibility of the network samples is so high that the Pincus blob concept is applicable. We have noticed that the above two conditions can be satisfactorily realized in a polymer network which is prepared by end- linking reaction in solution at a low polymer concentration with the precursor chains having a narrow size distribution. Such a network has not only much fewer number of trapped entanglements than that prepared without solvent but also the network chains with the conformation identified as randomcoil ($D = 2$). Furthermore, the network can possess a high extensibility due to fewer number of trapped entanglements which act in a similar way to chemical crosslinks against external mechanical forces.

In this study, we experimentally examine equation (1) by using the end-linked network prepared in solution at a relatively low concentration. On the basis of the experimental confirmation of the validity of equation (1), we analyze the $\sigma_e - \lambda$ relations of the deswollen network using equation (1) in order to estimate the fractal dimension of supercoiled conformation. We have prepared the network samples using the precursor chains with the narrow size distribution to eliminate the effects of the size distribution of network chains on the $\sigma_e - \lambda$ relations of the networks. (The precursor chains used in our previous study [12] had a finite size distribution.)

2 Experimental

The polymer network samples were prepared by end-linking reaction in distilled toluene between vinyl-terminated polydimethylsiloxane (PDMS) precursor chains and tetrakisdimethylsiloxysilane ($Si(OSi(CH_3)_2H)_4$). The end-linking was made by hydrosilylation reaction at 75 °C for 3 days. The precursor PDMS was obtained by the fractionation of the commercial vinyl-terminated PDMS (Chisso Co., Japan) using a mixture of 2-butanone and methanol as the solvent. The values of M_n and M_w/M_n for the precursor PDMS measured by gel permeation chromatography were 9.9×10^4 and 1.2 where M_w and M_n are the weight- and number-average molecular weights, respectively. The deswollen networks were obtained by evapolating toluene completely from the PDMS gels in the air. The experimental details of the preparation of deswollen networks are referred in reference [12]. The uniaxial elongation of the network samples with the initial lengths of *ca.* 10 mm were conducted at room temperature under the constant crosshead speed of 10 mm/min. It was experimentally checked that the elongation was made at quasi-elastic equilibrium condition under which the effects of stress relaxation on the $\sigma_e - \lambda$ relations can be neglected.

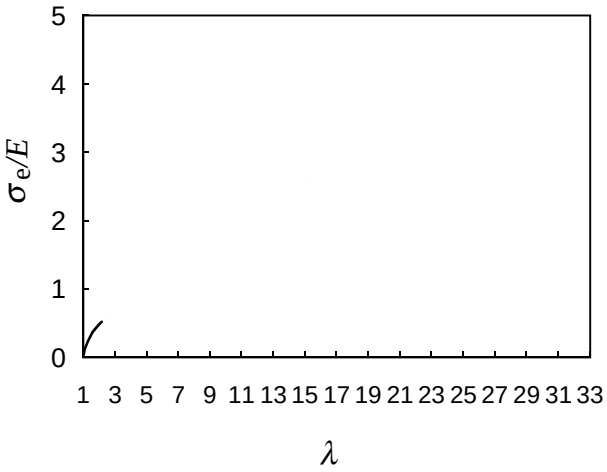

Fig. 1. Normalized stress (σ_e/E) - elongation (λ) curves of PDMS networks. σ_e and E are the engineering stress and initial Young's modulus, respectively. Bold solid line for the network prepared in bulk state ($\phi = 1$); dash-dot and solid lines for the networks prepared at $\phi = 0.10$ before and after deswelling, respectively. M_n and M_w/M_n of precursor PDMS for the networks prepared at $\phi = 1$ and 0.10 are 9.9×10^4 and 1.2, respectively; dotted line for the deswollen network prepared at $\phi = 0.09$ in previous study [12] in which M_n and M_w/M_n of precursor PDMS are 2.8×10^4 and 1.7, respectively.

3 Results and discussion

Figure 1 shows the $\sigma_e - \lambda$ relations of the four kinds of PDMS network including the deswollen network investigated in our previous study [12]. The stress in the figure is normalized by the initial Young's modulus (E) of each sample in order to compare exclusively the $\sigma_e - \lambda$ relations. It is seen that λ_{max} for the networks crosslinked in bulk state (namely, without solvent) remains two, while those for the networks crosslinked in the solutions at the low concentrations are far over 10. The large λ_{max} of the solution-crosslinked networks originates from a smaller number of trapped entanglements. It is also seen that the deswollen networks have the remarkable high λ_{max}, and that especially, λ_{max} for the deswollen network in

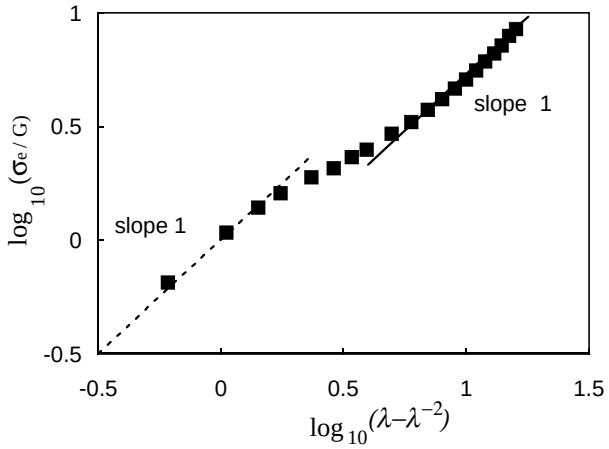

Fig. 2. Double logarithmic plots of σ_e/G *versus* $(\lambda - \lambda^{-2})$ for the PDMS network prepared at $\phi = 0.25$ in preparation state. σ_e, G and λ are the engineering stress, shear modulus and elongation ratio, respectively.

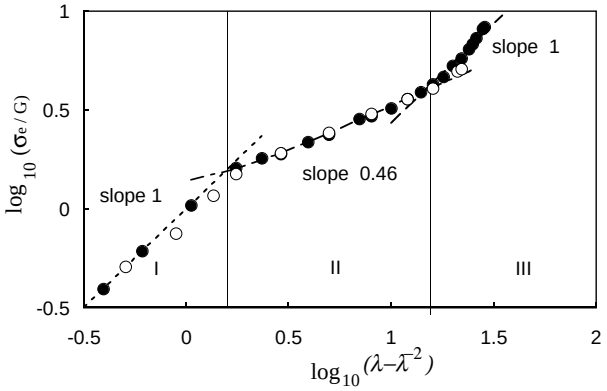

Fig. 3. Double logarithmic plots of normalized stress (σ_e/G) *versus* $(\lambda - \lambda^{-2})$ for the deswollen networks prepared at $\phi = 0.15$ (O) and $\phi = 0.10$ (•). σ_e, G and λ are the engineering stress, shear modulus and elongation ratio, respectively.

this study exceeds 30. It was experimentally checked that the latter network showed the perfect elastic recovery in unloading after the elongation $\lambda = 25$. The further enhancement of λ_{max} by deswelling is due to the reduction in the end-to-end distance of network chains in the undeformed state which is caused by a volume decrease of the gels in deswelling. The quantitative discussion for the emergence of high λ_{max} in a deswollen polymer network prepared at a low concentration is referred in references [9,12].

It can be also seen in Figure 1 that the deswollen network in previous study has the stronger λ dependence of σ_e than one in this study. The precursor PDMS chain used in the previous study has $M_n = 2.8 \times 10^4$ and $M_w/M_n = 1.7$, *i.e.*, it has smaller size and broader size distribution relative to the one in this study. The stronger λ dependence of σ_e is primarily attributed to the ultimate elongation effects on the short chain components involved in the precursor chains. For the detailed analysis, the employment of the $\sigma_e - \lambda$ relation for the deswollen network in this study is most preferable, since the sufficiently narrow size distribution of the precursor chains is realized.

Figure 2 shows the double logarithmic plots of σ_e/G *versus* $\lambda - \lambda^{-2}$ for the PDMS network prepared at $\phi = 0.25$ before deswelling, that is, just at preparation, where G and ϕ are the shear modulus and the volume fraction of precursor chains at crosslinking, respectively. The relation $G = E/3$ for incompressible materials was used. The networks prepared at $\phi < 0.25$ before deswelling were so soft that we failed to conduct their elongation measurements. Equation (1) is an asymptotic scaling law valid in the limit of very long network chains under strong extension. In order to test equation (1) using the network chains with a finite length under a moderate extension, we need to include the correction term $(1 - \lambda^{-3})$ due to lateral compression [9,18]. In the strong stretching region $\lambda > 2.5$, the contribution of this correction term can be safely neglected (*i.e.*, $\lambda - \lambda^{-2} \approx l$). As can be seen in the figure, the λ dependence of σ_e in the large deformation region $6 < \lambda < 16$ is well represented by $\sigma_e \sim \lambda^1$. Although toluene is a good solvent for PDMS, the excluded volume effects on the spatial correlation inside the network chain would be fully screened due to the fairly high overlapping of network chains at the polymer concentration concerned ($\phi/\phi^* \approx 15$ where ϕ^* is the polymer volume fraction at which the overlapping of the precursor chains begins) [19]. Consequently, the correlation correlation inside the network chain is described by Gaussian chain statistics, *i.e.*, randomcoil nature. It is found that equation (1) for randomcoil ($D = 2$) coincides with the experimental λ dependence of σ_e at large deformations. This agreement supports the validity of the Pincus blob concept.

The classical theory of rubber elasticity [18] predicts the stress-λ relation of the network composed of Gaussian chains as $\sigma_e/G = \lambda - \lambda^{-2}$. This prediction is represented by the dotted straight line with the slope of unity passing the origin in the figure. The experimental data in the region $\lambda > 2$ deviate downward from the prediction by classical theory, though they fall on the straight line in the region $\lambda < 2$. The downward deviation from the classical theory is qualitatively interpreted as in the case of the additional C_2 term in the Mooney-Rivlin equation [6,19]. The major origin of the deviation from the classical theory has often been attributed to the effects of trapped entanglements which are neglected in the classical theory. The downward deviation in the moderate deformation region may be due to a non-negligible amount of trapped entanglements in the network prepared at $\phi = 0.25$. However, it should be noted that the experimental result $\sigma_e \sim \lambda^1$ in $l > 6$ agrees with the power law for $\sigma_e - \lambda$ relation in large λ region predicted by the classical theory.

Figure 3 shows the plots of log (σ_e/G) *versus* log $(\lambda - \lambda^{-2})$ for the deswollen networks prepared at $\phi = 0.15$ and $\phi = 0.10$. As in the case of Figure 2, $(\lambda - \lambda^{-2})$ including the correction term, instead of λ, is used here. It is seen that both the data coincide with each other over the whole λ, although λ_{max} is larger for the networks prepared at $\phi = 0.10$. This suggests that the $\sigma_e - \lambda$ relation is typical of the deswollen networks composed of supercoiled chains. The λ dependence of σ_e can be divided

into the three regions as indicated in the figure. Region I ($1 < \lambda < 1.6$) is the small deformation region in which the data points fall on the straight line with the slope of unity through the origin, suggesting that λ dependence of σ_e is well described by the prediction of the classical theory for rubber elasticity. In region II, the data fall on the straight line with the slope of 0.46, indicating that the λ dependence of σ_e obeys $\sigma_e \sim \lambda^{0.46}$. In region III, the λ dependence of σ_e is represented by $\sigma_e \sim \lambda^{1.0}$. It should be noted that these power laws hold in the wide λ regions ($1.6 < \lambda < 16$ and $16 < \lambda < 31$, respectively).

We consider the region II as the disentanglement process of the supercoiled structure, and the region III as the elongation process after the complete disentanglement of the supercoiled structure. The Pincus blob concept predicts $\sigma_e \sim \lambda^{0.5}$ for the elongation of a densely packed conformation with $D = 3$. This prediction is close to the experimental result in the region II. We numerically obtain 3.2 for D by applying directly the experimental result to equation (1). This suggests that supercoil is a more strongly contracted conformation relative to randomcoil. A polymer chain in globule state [1,5] and in an array of obstacles (PCAO) with excluded volume effects [3–5] are the examples for the models and concepts for the strongly collapsed polymer chains with $D = 3$.

The crossover in the λ dependence of σ_e in the region II and III agrees well with the prediction by Obukhov *et al.* [9] that after the complete disentanglement of the supercoiled structure, the λ dependence of σ_e becomes the randomcoil type, which emerges as the change in the scaling exponent from $1/(D-1)$ to unity. Their prediction for the λ dependence of σ_e for the deswollen networks with high extensibility (see Fig. 7 in Ref. [9]) fairly well reproduces the features in Figure 1 such as the weak λ dependence of σ_e and the crossover in the scaling exponent, except that the exponent in Region II in their prediction is 1/3. The difference in the exponent in Region II results from that they considered $D = 4$ for supercoiled structure. The elongation $\lambda_c \approx 16$ at the crossover in the λ dependence of σ_e is interpreted as the elongation necessary for disentangling supercoil completely. According to Picus blob concept, the number of Pincus blobs increases (*i.e.*, the number of monomers in a Pincus blob (g_p) decreases) with increasing λ during the disentanglement process, and the power law behavior for a certain D continues until g_p reduces to a critical value (g_{pc}) corresponding to the complete disentanglement. Under the assumption of the affine displacement of crosslinking points in deswelling and elongation, λ_c is related to g_{pc} as

$$\lambda_c \approx \left(\frac{N}{g_p}\right)^{1/2} \phi^{-1/3} \qquad (2)$$

where N is the number of monomers in a precursor chain. Obukhov *et al.* [9] calculated λ_c assuming $g_{pc} = N_e$ where N_e is the number of monomers between neighboring entanglement couplings. However, $\lambda_c \approx 7.5$ which is obtained using $g_{pc} = N_e$ and $N/N_e \approx 12$ is much smaller than the experimental value. (Here, $M_e = 8100$ for PDMS [20] was used where M_e is the molecular weight between entanglements.) This implies that the correlation characteristic of supercoil is preserved up to the fairly larger elongation than their expectation, *i.e.*, $g_{pc} < N_e$. Actually, $g_{pc} \approx (1/5)N_e$ is obtained using the experimental value of λ_c.

The differences in D for supercoil and g_{pc} between our experimental results and Obukhov *et al.*'s predictions may originate from that the length of the network strand (*i.e.*, the precursor chain) in this study ($N/N_e \approx 12$) is not enough long to satisfy the condition in their model treating supercoil as a random double-folded treelike configuration. They treated the deswollen network whose network strand is extremely long [9]. In order to discuss this problem, we need to investigate the dependence of D for supercoil on the length of network strand N. It is expected that D approaches 4 asymptotically with the increase in N, if their prediction is valid.

Furthermore, in order to elucidate the more details of the spatial correlation for supercoil, another experimental methods such as the small angle neutron scattering experiments for the labelled network chains are necessary. This is the future subject in our study.

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