

博士論文 (要約)

Strain Energy Density Function of Polymer Gels with Controlled
Network Structure

(構造の制御された高分子ゲルの歪エネルギー密度関数)

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Introduction

Elastomeric Polymer networks exhibit reversible large deformability and markedly non-linear stress-elongation relationship stemming from the entropic elasticity. This unique elasticity gives them a special entity in the academic and engineering field. Full understanding of the non-linear stress-elongation relationship of polymer networks is one of the ultimate goals of polymer science.

The stress-elongation relationship of polymer networks is governed by the strain energy density function (W); the nominal stress (σ_i) is the partial derivative of W with respect to the principal stretch ratio (λ_i). In general, the W function is mainly influenced by two factors: the initial network structure and the subsequent swelling and deswelling. In particular, polymer gels, which are prepared in the various solvent conditions, have a strong dependence of its mechanical properties on the swelling and deswelling. Although there have been many studies to investigate the molecular origin of the W functions in the past half century, the full understanding of the W function remains incomplete mainly due to the heterogeneities in the networks.

In general, polymer networks are inherently heterogeneous; the heterogeneous distribution of the polymer chains, dangling chains, elastically ineffective loops and trapped entanglements. These heterogeneities are uncontrollable, making it difficult to evaluate accurate structural parameters, such as the polymerization degree of a network strand and the density of crosslinks. The ambiguity of structural parameters inhibits us from providing a definite basis for the understanding of the molecular interpretation of the W function. Thus, the experiments using homogeneous networks with precisely controlled structures are needed.

Recently, we have successfully designed and fabricated a “Tetra-PEG gel” achieving extremely homogeneous network, which is formed by the AB type crosslink-coupling of two mutually reactive tetra-arm polyethylene glycol. Our previous works showed that the

Tetra-PEG gel extremely suppresses these heterogeneities, and strongly suggest that the Tetra-PEG gel is a candidate for the model system with controlled network structures. In my thesis, I employed the Tetra-PEG gel and systematically investigated the effects of the initial network structure and the swelling and deswelling on the W functions.

Effects of Network Structure in As Prepared State on Strain Energy Density Function¹

I discuss here the W function of the as-prepared Tetra-PEG gels. I prepared the Tetra-PEG gels, and performed the biaxial stretching for each gel sample. General biaxial stretching, where the strains can be varied in two directions independently, can cover all the physically accessible deformation regions, and provide more information for the

W function than the uniaxial deformation. Figure 1 shows the stress-elongation relationships under the equibiaxial stretching (EB), pure shear (PS) and unequibiaxial stretching (UB). σ_x and σ_y represent the stress in x and y directions, respectively. Conventional molecular models for the homogeneous networks could not describe the experimental results (FIG. 1 (a)). These deviations from the model predictions were attributed to the strain-coupling between the different principal axes. The strain-coupling was influenced by the network fraction including the dangling chains, suggesting that the strain-coupling originates from the friction

of the network accompanied with the macroscopic deformation. I extended the Gent model,² which is one of the conventional models considering the finite extensibility, and successfully

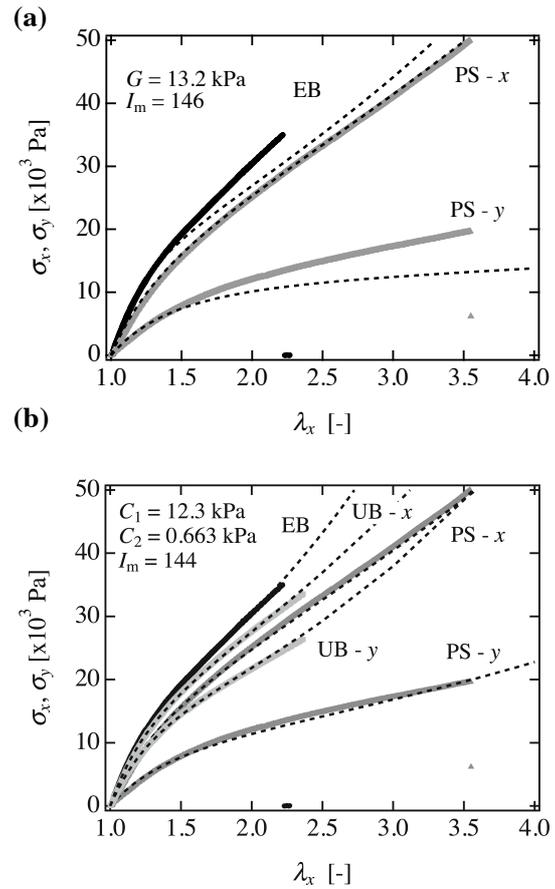


FIG. 1. Nominal stress–elongation relations for Tetra-PEG gel under equibiaxial stretching (EB), pure shear (PS), and unequibiaxial stretching (UB). The dashed lines are fitting results of (a) the Gent model and (b) the Extended Gent model.

described the experimental results (Extended Gent model) (FIG. 1 (b)). This model includes three parameters: the number of network strands, the strength of strain-coupling between different axes, and the maximum value of the first invariant.

Effects of Swelling and Deswelling on Strain Energy Density Function ³

I discuss the effects of swelling and deswelling on the W function of Tetra-PEG gels by varying the polymer volume fraction of interest (ϕ_m). First, I investigated the stress-elongation behavior under the uniaxial deformation. The ϕ_m -dependence of the elastic modulus (E_m) exhibited a crossover at a certain polymer volume fraction (ϕ_c) due to large contraction of the network strands (supercoiling) accompanying deswelling. The theoretical model considering the excluded volume effect of the network strand at preparation state ⁴ successfully described the ϕ_m -dependence of the elastic modulus (FIG. 2 (a)). I estimated the fractal dimension of network strands (D_f) by analyzing the stress-elongation relationships at high stretching using Pincus blob concept. ⁵ In the supercoiling region, D_f increased with an increase in ϕ_m , suggesting that the gyration radius of network strands, which is proportional to N^{1/D_f} , decreases with deswelling in affine manner (FIG. 2 (b)). Here, N represents the polymerization degree of the network strand. Furthermore,

I plan to perform the biaxial stretching for the swollen and deswollen Tetra-PEG gels, and to

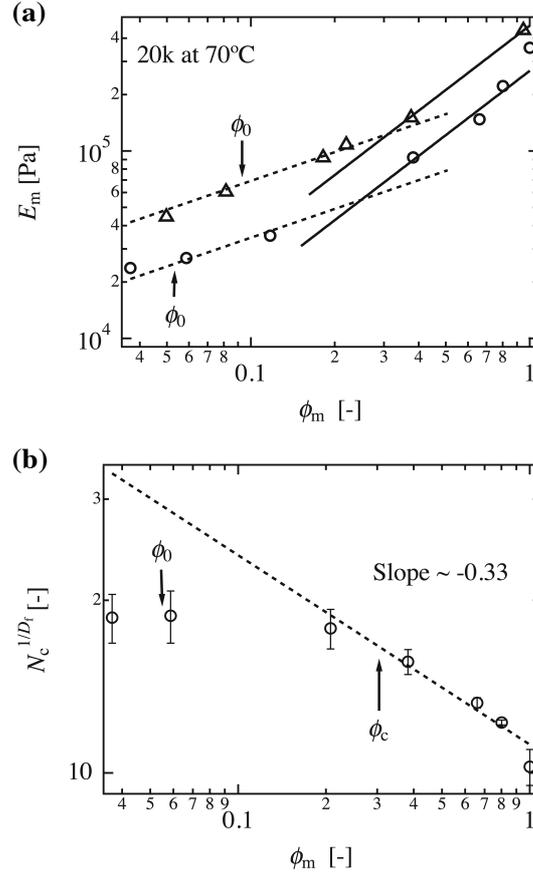


FIG. 2. (a) The ϕ_m -dependence of the elastic modulus of interest (E_m) for 20k Tetra-PEG gels at 70°C. The dashed and solid lines represent the theoretical predictions. (b) Double logarithmic plot of N^{1/D_f} against ϕ_m . The dashed line corresponds to a relationships of $N^{1/D_f} \sim \phi_m^{-1/3}$.

investigate the effects of the swelling and deswelling on the W function using the extended Gent model.

Conclusions

I systematically investigated the effects of the initial network structure and the swelling and deswelling on the W functions. The results of the experiments for the as prepared gels are summarized as follows: (1) Conventional molecular models could not describe the experimental results under the general biaxial stretching due to the strain-coupling between the different principle axes; (2) The strain-coupling was influenced by the network fraction including the dangling chains, suggesting that the strain-coupling originates from the network friction; (3) I successfully deduced the W function for the Tetra-PEG gels with three parameters: the number of network strands, the strength of strain-coupling between different axes, and the maximum value of the first invariant. The results of the experiments for the swollen and deswollen gels are summarized as follows: (1) A crossover in the ϕ_m -dependence of E_m occurs due to a pronounced supercoiling; (2) the ϕ_m -dependence of D_f indicates that the gyration radius of the network strands decreases with a reduction of gel dimension in affine manner. These results can be a guideline for material design of polymer networks.

References

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