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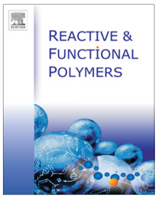

Theory of volume phase transition of slide-ring gels

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ABSTRACT

Volume phase transition is a phenomenon in which gels drastically swell or shrink with an infinitesimal change in the external environment. This behavior is well explained by the Flory–Rehner–Tanaka theory. However, some assumption in the theory breaks down in a slide-ring gel composed of grand canonical chains in which the segment number between cross-linking junctions can change. The stress–strain behavior of the slide-ring gel is in a qualitative agreement with the free junction model, in which the segment number changes to maximize the entropy under the condition that the total sum of the segment number is constant. However, the model cannot work well to isotropic swelling of the slide-ring gel. To describe the volume phase transition of the slide-ring gel, we propose a new theory based on the free junction model with the effects of dangling strands, uncross-linked cyclic molecules (free rings), and high elongation. As a result, it turns out that the exchange of segments between effective and dangling strands leads to the suppression of the volume phase transition in the highly cross-linked gel and the promotion in the loosely cross-linked one. The suppression and promotion of the volume phase transition became more obvious as free rings decreased.

1. Introduction

Volume phase transition is a phenomenon in which gels drastically swell or shrink with an infinitesimal change in the external environment, such as the chemical composition of the solvent mixture [1–3], temperature [4–6], pH [2], salt concentration [7], electric field [8], ultraviolet [9], and visible light [10]. It is experimentally and theoretically established that the discontinuous transition occurs in chemical gels when they have a higher degree of ionization than a critical value [2,6]. This behavior was well explained by the Flory–Rehner–Tanaka theory [2,11], in which the effect of mixing, the entropy of counterions, and the rubber elasticity are all considered. It is natural in the chemical gel that the chain length, or the segment number, between cross-linking junctions is constant during deformation in the calculation of the rubber elasticity.

However, the segment number between cross-linking junctions is not necessarily constant in all kinds of gels. For instance, the segment number between cross-linking junctions changes with deformation in slide-ring (SR) gels [12]. The SR gel is made from polyrotaxane [13] (PR), in which cyclic molecules are threaded on an axis polymer chain capped by bulky end groups. Schematic illustrations of PR and the SR gel are shown in Fig. 1. Cyclic molecules form movable cross-linking junctions sliding along the axis polymer chains. The internal stress is reduced by exchange among highly extended and shrunken chains through cross-linking junctions. As a result, the SR gel shows novel mechanical and swelling properties [14–19] such as high extensibility over 20 times in length, huge swellability up to 24,000 times by weight, and low Young's modulus. It is also reported that the SR gel shows anomalous stretching-induced swelling behavior [20,21].

The free junction model has been proposed to describe the *J*-shaped stress–strain curve characteristic of the SR gel qualitatively [17]. It assumes that the polymer network behaves as the grand canonical chains: each segment number of three Gaussian chains can change with deformation to maximize the entropy under the constraint condition that the total sum of the segment number is constant. Whereas the free junction model gives us an uniaxial deformation behavior quite different from the fixed junction model, it becomes equivalent to the fixed junction model in isotropic swelling, where all chains deform on the same elongation ratio without change in the segment numbers. When we consider the swelling–shrinking behavior of the SR gel, we should incorporate some important factors other than the exchange of chains over cross-linking junctions in the free junction model. Firstly, the SR gel has many dangling strands. One PR yields two dangling strands in the SR gel as shown in Fig. 1b. Different from the chemical gel, dangling strands can slide to elastically effective network strands between cross-linking junctions and thereby affect the swelling and elastic behavior substantially in the SR gel. Secondly, the effect

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of uncross-linked cyclic molecules (free rings) should be taken into account. All cyclic molecules are not cross-linked in the SR gel. Free rings yield alignment entropy from the distribution on a backbone polymer as large as the well-known conformational entropy of polymer chains [22]. Cyclic molecules cannot pass through cross-linking junctions, so that they tend to suppress the sliding motion of dangling strands through cross-linking junctions. In other words, free rings affect the chemical potential of grand canonical strands in the SR network considerably. Thirdly, we ought to treat polymers as non-Gaussian chains for highly swelling gels.

Our purpose in the present study is to modify the theoretical network model of the SR gel with the effects of dangling strands, free rings, and non-Gaussian chains. We propose a generalized free junction model, which significantly simplifies the modification of the free energy of chains or the network structure to obtain the elastic stress of the SR gel. The modified free junction model is applied to the volume phase transition of the SR gel, calculating the free energy and the swelling–shrinking curve. We show the numerically calculated swelling–shrinking behavior in two typical cases: highly and loosely cross-linked gels.

2. Theory

2.1. Generalization of the free junction model

The free junction model has two assumptions: (a) the segment number of a strand changes to minimize the free energy and (b) the segment number of each PR is constant. These two assumptions are expressed from the method of Lagrange multipliers as

$$\frac{\partial F}{\partial N_p} = \mu \quad \text{for each } p \tag{1}$$

$$\sum_p N_p = N_{\mathrm{PR}} \tag{2}$$

where F is the total free energy, N_p the segment number of pth strand in a PR, μ the Lagrange multiplier as the chemical potential of a strand in a PR, and N_{PR} the total segment number of a PR. The total free energy is given as a sum of the free energy of all strands:

$$F = \sum_{\text{all PRs}} \sum_p F_p \tag{3}$$

where F_p is the free energy of pth strand in a PR. Since it is natural that the free energy of a strand should not depend explicitly on the segment number of other strands, Eq. (1) is written as

$$\mu_p \equiv \frac{\partial F_p}{\partial N_p} = \mu \quad \text{for each } p \tag{4}$$

where μ_p is the chemical potential of pth strand in a PR. This means that the segment number of each strand is determined to equalize the chemical potential of each strand in a PR. The segment number of each strand is obtained from Eqs. (2) and (4).

Since the free energy of the free junction model depends explicitly on the segment number of strands, the engineering stress σ_j in the x_j-direction (j = 1, 2, 3) is given by

$$\sigma_j = \frac{1}{V_0}\left(\sum_{k=1}^{3} \frac{\partial F}{\partial \lambda_k}\frac{\partial \lambda_k}{\partial \lambda_j} + \sum_{\text{all PRs}} \sum_p \frac{\partial F}{\partial N_p}\frac{\partial N_p}{\partial \lambda_j}\right) \tag{5}$$

where V_0 is the volume of a gel in the reference state and λ_j the ratio of the dimensions along the x_j-axis in the undeformed and deformed states. The fixed junction model does not have the second term since the segment number is always constant. In the free junction model, however, the second term necessarily becomes zero from Eqs. (1) and (2):

$$\sum_p \frac{\partial F}{\partial N_p}\frac{\partial N_p}{\partial \lambda_j} = \mu \frac{\partial N_{\mathrm{PR}}}{\partial \lambda_j} = 0 \tag{6}$$

Hence

$$\sigma_j = \frac{1}{V_0} \sum_{k=1}^{3} \frac{\partial F}{\partial \lambda_k}\frac{\partial \lambda_k}{\partial \lambda_j} \tag{7}$$

This equation means that the stress of the free junction model can be calculated as if the segment number were constant. The engineering stress is obtained by substituting the segment number N_p obtained from Eqs. (2) and (4) into Eq. (7). Incidentally Eq. (7) is coincident with the engineering stress of the fixed junction model when the segment number is always constant.

2.2. Free energies and chemical potentials of non-Gaussian chains and cyclic molecules

The distribution function of a non-Gaussian chain is given by [23]

$$P(R, N) = \frac{1}{4\pi b^3 N^3 I_2(N)} \exp\left[-N\mathcal{K}\left(\frac{R}{bN}\right)\right] \tag{8}$$

where R is the end-to-end distance, N the segment number (the number of Kuhn monomer), and b the segment length (the Kuhn length), and

$$\mathcal{K}(\alpha) \equiv \alpha\mathcal{L}^{-1}(\alpha) - \mathcal{M}(\mathcal{L}^{-1}(\alpha)) = \int_0^\alpha \mathcal{L}^{-1}(x)dx \tag{9}$$

$$\mathcal{M}(\beta) \equiv \ln\frac{\sinh\beta}{\beta} = \int_0^\beta \mathcal{L}(y)dy \tag{10}$$

$$\mathcal{L}(\beta) \equiv \coth\beta - \frac{1}{\beta} \tag{11}$$

$$I_2(N) \equiv \int_0^1 \alpha^2 \exp[-N\mathcal{K}(\alpha)]d\alpha \tag{12}$$

It is assumed that chains are Gaussian in the reference state: $R_0 = bN_0^{1/2}$, where R_0 and N_0 are the end-to-end distance and the segment number in the reference state, respectively. The free energy of a non-Gaussian chain elongated by the factor of λ whose segment number becomes N is given by

$$\begin{aligned}\frac{F_{\mathrm{NG}}(\lambda, N)}{k_{\mathrm{B}}T} &= -\ln P(\lambda R_0, N)4\pi(\lambda R_0)^2 d(\lambda R_0)\\ &= N\mathcal{K}\left(N_0^{-1/2}\frac{N_0}{N}\lambda\right) - 3\ln\frac{N_0}{N}\lambda - \ln I_2(N) + \text{const}\end{aligned} \tag{13}$$

where k_{B} is the Boltzmann constant and T the absolute temperature. The chemical potential of non-Gaussian chain is given by

$$\begin{aligned}\frac{\mu_{\mathrm{NG}}(\lambda, N)}{k_{\mathrm{B}}T} &= \frac{1}{k_{\mathrm{B}}T}\frac{\partial F_{\mathrm{NG}}}{\partial N}\\ &= -\mathcal{M}\left(\mathcal{L}^{-1}\left(N_0^{-1/2}\frac{N_0}{N}\lambda\right)\right) + \frac{3}{N} - \frac{1}{I_2(N)}\frac{dI_2(N)}{dN}\end{aligned} \tag{14}$$

Uncross-linked cyclic molecules are confined between cross-linking junctions or end-capping groups. The distribution function of n uncross-linked cyclic molecules confined in n_{t} lattice sites is given by the binomial distribution function [22]:

$$P(n, n_{\mathrm{t}}) = \frac{1}{2^{n_{\mathrm{t}}}}\frac{n_{\mathrm{t}}!}{n!(n_{\mathrm{t}} - n)!} \tag{15}$$