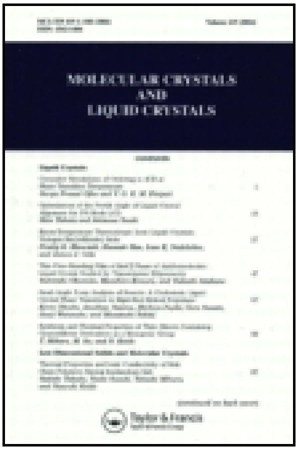

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Volume Phase Transitions of Gels in Liquid Crystal Solvents

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Volume Phase Transitions of Gels in Liquid Crystal Solvents

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A simple mean field theory is introduced to describe volume phase transitions of gels dissolved in a liquid crystal solvent. We predict that the gel shows the second-order volume phase transition at the nematic-isotropic transition temperature T_{NI}° of the pure liquid crystals existing outside of the gel. Below T_{NI}°, the gel is condensed due to the nematic ordering of the pure liquid crystals. We also find the first-order volume phase transition in the isotropic phase above T_{NI}°.

Keywords: Swelling of gel; liquid crystal solvents; volume phase transitions; mean field theory

1. INTRODUCTION

Volume phase transitions of gels in an isotropic solvent have been intensively studied. A simple mean field theory based on the Flory model gives qualitatively correct descriptions of many observed properties in the volume phase transition of gels [1–4] and the coil-globule transition of a single polymer chain [5–9]. These collapse transitions are closely related to the phase separations in solutions of free chains. The mean field theory of the Flory type has shown that the first order volume transition from a swollen gel to a condensed gel takes place as temperature is decreased [1]. At high temperatures, the entropy of mixing dominates and so the gel swells. As temperature is decreased, the gel collapses into a condensed state at a critical temperature where the unfavorable solute-solvent interaction dominates.

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The mechanism of this phase transition is similar to that of the gas–liquid transition.

In contrast to the gels immersed in isotropic solvents, the nematic solvents such as liquid crystals can play an important role for the volume changes of gels. In these systems, the equilibrium volume of the gels is determined by both the orientational order parameter of liquid crystals and the concentration.

In the binary mixtures of a flexible polymer and a liquid crystal, the nematic-isotropic phase separation and the isotropic–isotropic one with an upper critical solution temperature have been observed on the temperature-concentration plane [10–21]. Typical examples are the mixtures of (*p*-ethoxybenzylidene)-*p*-*n*-butylaniline (EBBA) and polystylene (PS) and the mixtures of 4-cyano-4′-*n*-heptylbiphenyl (7CB) with PS. Then we can expect the volume changes of gels in a liquid crystal solvent when the temperature is changed.

Recently we have presented a simple theory to describe phase separations in binary mixtures of a linear flexible polymer and a liquid crystal [19]. The aim of this paper is to extent our theory to networks (gels) in liquid crystal and is to calculate the degree of swelling of the gel as a function of temperature. We find that the gel exhibits the second-order volume phase transition at the nematic-isotropic transition temperature T_{NI}° of the pure liquid crystals existing outside of the gel.

2. EQUILIBRIUM SWELLING OF A NETWORK IN A LIQUID CRYSTAL SOLVENT

We consider a gel dissolved in a liquid crystal solvent. We here assume that the gel consists of sufficiently flexible subchains which do not contribute to the nematic ordering. We here focus on the isotropic deformation of the gel. The anisotropic deformation is important for gels under an external field [20, 22] and for gels consisting of liquid crystalline polymer chains. Let n be the number of segments between crosslinks and n_r be the axial ratio of the liquid crystal. Swelling and collapse of the gel can be characterized by the expansion factor $Q = V/V_0$, where V and V_0 are the final and initial volume of the gel, respectively. Another equivalent expression for the expansion factor is

$$Q = \phi_0/\phi, \tag{2.1}$$

where ϕ_0 and ϕ are the volume fraction of subchains in the initial and the final state of the gel, respectively. Let N_g and N_r be the number of subchains and liquid crystal solvents, respectively. The volume fraction of the gel is given by $\phi = nN_g/N_t$, where N_t $(=nN_g + n_rN_r)$ is the number of the total lattice sites existing inside of the gel.

The free energy of gels in a liquid crystal solvent is given by

$$F = F_{\mathrm{el}} + F_{\mathrm{mix}} + F_{\mathrm{nem}}. \tag{2.2}$$

The first term F_{el} in Eq. (2.2) shows the elastic free energy of subchain deformation and is given by [23]

$$\beta F_{\mathrm{el}} = N_g\left[\frac{3}{2}(Q^{2/3} - 1) - \frac{2}{J}\ln Q\right], \tag{2.3}$$

where $\beta \equiv 1/k_BT$; T is absolute temperature, k_B is the Boltzman constant, J is the network functionality and we here take $J = 4$.

The second term F_{mix} describes the free energy of mixing of the gel with a solvent molecule. In the framework of the Flory-Huggins theory, the free energy is given by [23]

$$\beta F_{\mathrm{mix}} = N_t\left[\frac{1-\phi}{n_r}\ln(1-\phi) + \chi\phi(1-\phi)\right], \tag{2.4}$$

where $\chi(\propto 1/T) > 0$ shows the isotropic (Flory-Huggins) interaction parameter between subchain and solvent molecules.

The third term F_{nem} shows the free energy for nematic ordering. To describe the nematic behavior of liquid crystal solvents, we take into account the excluded volume interactions [24] and the orientation-dependent attractive interactions [25, 26] between liquid crystals. The free energy F_{nem} is given by [19]

$$\begin{aligned}\beta F_{\mathrm{nem}} = N_t\Bigg[&\frac{(1-\phi)}{n_r}\int f(\theta)\ln 4\pi f(\theta)d\Omega \\ &-\frac{1}{2}\chi_a S_i^2(1-\phi)^2 + (\rho - 1)(1-\phi)^2\Bigg],\end{aligned} \tag{2.5}$$

where χ_a is the attractive (Maier-Saupe) interaction parameter between liquid crystals, $d\Omega \equiv 2\pi\sin\theta\, d\theta$, θ is the angle between the liquid crystal and director, and the $f(\theta)$ is the normalized distribution of the liquid crystal over various orientations. In the isotropic phase, we have $f(\theta) = 1/(4\pi)$. The order parameter S_i of the liquid crystal existing inside of the gel is given by

$$S_i = \int P_2(\cos\theta)f(\theta)d\Omega, \tag{2.6}$$

and the function ρ is defined by

$$\rho \equiv \frac{4}{\pi}\int\int \sin\gamma(\theta,\theta')f(\theta)f(\theta')d\Omega d\Omega'. \tag{2.7}$$

The last term of Eq. (2.5) shows the excluded volume interaction between liquid crystals.

The orientation distribution function $f(\theta)$ is determined by the minimizing the free energy (2.5) with respect to $f(\theta)$. This leads to the integral equation

$$\begin{aligned}\ln 4\pi f(\theta) &= C + n_r\chi_a S_i(1-\phi)P_2(\cos\theta)\\ &\quad -\frac{8}{\pi}n_r(1-\phi)\int \sin\gamma(\theta,\theta')f(\theta')d\Omega',\end{aligned} \tag{2.8}$$

where the constant C is determined by the normalization condition

$$\int f(\theta)d\Omega = 1. \tag{2.9}$$

We here expand the kernel $\sin\gamma$ in Legendre polynomials:

$$\sin\gamma = \frac{\pi}{4} - \frac{5\pi}{32}P_2(\cos\theta)P_2(\cos\theta'), \tag{2.10}$$

$$P_2(\cos\theta) = \frac{3}{2}\left(\cos^2\theta - \frac{1}{3}\right), \tag{2.11}$$

and substituting Eq. (2.10) into (2.8) we obtain

$$f(\theta) = \frac{1}{Z}\exp[\eta_i S_i P_2(\cos\theta)], \tag{2.12}$$

where

$$\eta_i \equiv \left(\chi_a + \frac{5}{4}\right)n_r(1-\phi). \tag{2.13}$$

From Eq. (2.9) the constant Z is given by

$$Z = 2\pi\, I_0\, [\eta_i S_i], \tag{2.14}$$

and the function $I_0[\eta S]$ is defined as

$$I_m[\eta S] \equiv \int_0^1 \left[\frac{3}{2}\left(\cos^2\theta - \frac{1}{3}\right)\right]^m \exp\left[\frac{3}{2}\eta S\left(\cos^2\theta - \frac{1}{3}\right)\right] d(\cos\theta), \qquad (2.15)$$

$m = 0,1,2,\ldots$. From Eqs. (2.6) and (2.12), the orientational order parameter S_i of the liquid crystals existing inside of the gel is determined by the self-consistent equation

$$S_i = I_1[\eta_i S_i]/I_0[\eta_i S_i], \qquad (2.16)$$

and $\sigma \equiv \int f(\theta) \ln 4\pi f(\theta)\, d\Omega$ and ρ are given as a function of S_i follows:

$$\sigma = \eta_i S_i^2 - \ln(I_0[\eta_i S_i]), \qquad (2.17)$$

$$\rho = 1 - \frac{5}{8} S_i^2. \qquad (2.18)$$

Substituting Eqs. (2.17) and (2.18) into (2.5), the free energy F_{nem} can be expressed as

$$\beta F_{\text{nem}} = N_t \left[\frac{1}{2}\left(\chi_a + \frac{5}{4}\right) S_i^2 (1-\phi)^2 - \frac{(1-\phi)}{n_r} \ln(I_0[\eta_i S_i])\right]. \qquad (2.19)$$

The chemical potential of the liquid crystals existing inside of the gel is given by

$$\begin{aligned}\beta\mu_r(\phi, S_i) &= \beta(\partial F/\partial N_r)_{N_g,T} \\ &= \frac{\phi_0}{n}(Q^{-1/3} - Q^{-1}) + \frac{1}{n_r}(\phi + \ln(1-\phi)) + \chi\phi^2 \\ &\quad + \frac{1}{2}\left(\chi_a + \frac{5}{4}\right) S_i^2 (1-\phi)^2 - \frac{1}{n_r} \ln\,(I_0[\eta_i S_i]), \qquad (2.20)\end{aligned}$$

where ϕ is uniquely related to the expansion factor Q through the relation (2.1). The order parameter S_i is given as a function of Q by solving the self-consistent equation (2.16).

The chemical potential of the pure liquid crystals existing outside of the gel is given by substituting $\phi = 0$ into Eq. (2.20) as follows;

$$\beta\mu_r^\circ(S_b) = \frac{1}{n_r}\left[\frac{1}{2}\eta_b S_b^2 - \ln(I_0[\eta_b S_b])\right], \qquad (2.21)$$

where

$$\eta_b \equiv \left(\chi_a + \frac{5}{4}\right) n_r, \tag{2.22}$$

and the order parameter S_b of the pure liquid crystals is determined by the self-consistent equation

$$S_b = I_1[\eta_b S_b]/I_0[\eta_b S_b], \tag{2.23}$$

as a function of temperature.

The equilibrium swelling ratio Q of the gel can be obtained from the balance among the liquid crystals existing outside and inside of the gel:

$$\mu_r^\circ(S_b) = \mu_r(\phi, S_i). \tag{2.24}$$

Substituting Eqs. (2.20) and (2.21) into (2.24), we can numerically solve the swelling ratio of gels as a function of temperature.

3. NUMERICAL RESULTS AND DISCUSSION

For numerical calculations, we introduce the temperature paramter τ defined by $\tau \equiv 1/\chi$ $(= k_B T/U_0)$. We then have five parameters characterizing our systems; n, the number of segments between crosslinks; n_r, the axial ratio of a liquid crystal; ϕ_0, the initial concentration of a gel; χ_a, the orientation-dependent interaction (Maier-Saupe) parameter between liquid crystals; $\chi = 1/\tau$, the polymer-solvent interaction (Flory-Huggins) parameter. We here define the nematic interaction parameter $\alpha \equiv \chi_a/\chi$. We have fixed $\phi_0 = 0.01$ and $n_r = 2$ for a typical example.

Figure 1 shows the difference between the chemical potential (μ_r°) of the pure liquid crystals and that (μ_r) of the liquid crystals existing inside of the gel as a function of $\log(V/V_0)$ for $\alpha = 4.1$, $n = 100$. The temperature is changed near the nematic-isotropic transition temperature T_{NI}° of the pure liquid crystals existing outside of the gel. The vertical dotted lines show the nematic-isotropic transition of the liquid crystals existing inside of the gel. The right (left) hand side of the dotted line corresponds to the nematic (isotropic) gel. The equilibrium swelling ratio Q of the gel is determined by Eq. (2.24); $\mu_r - \mu_r^\circ = 0$. The value of Q is continuously decreased with decreasing temperature as shown in Figure 2.

Figure 2 shows the swelling ratio V/V_0 of the gel plotted against the reduced temperature T/T_{NI}°, for $n = 100$, 1000 with $\alpha = 4.1$. As temperature is decreased, the second-order volume phase transition takes place at T_{NI}°.

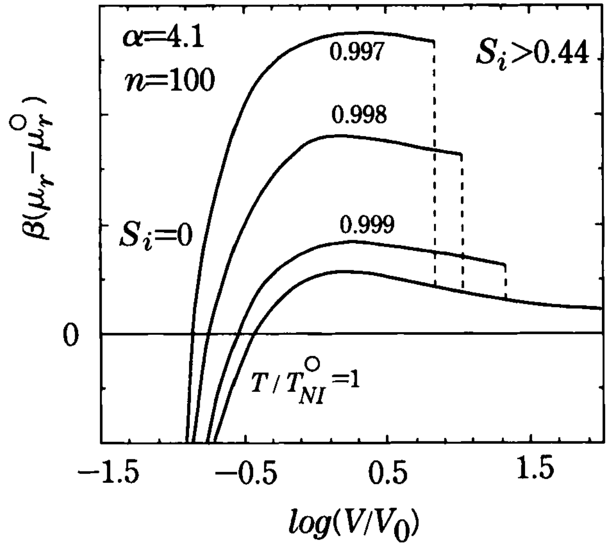

FIGURE 1 The differences between the chemical potential (μ_r°) of the pure liquid crystals and that (μ_r) of the liquid crystals existing inside of the gel as a function of log(V/V_0) for α = 4.1 and n = 100. The equilibrium swelling ratio Q of the gel is determined by Eq. (2.24).

Below T°_{NI}, the gel collapse into a globule state. When $\alpha=4.1$, the phase diagram on the temperature-concentration plane for the binary mixture has the nematic-isotropic phase separation below T°_{NI} [19]. As shown in Figure 3, below T°_{NI}, the pure liquid crystal existing outside of the collapsed gel is in a nematic state. The liquid crystal in the collapsed gel, however, is in an isotropic state. The gel is condensed due to the nematic ordering of the liquid crystals existing outside of the gel.

Figure 4 shows the swelling ratio of the gel for $n=50$. The nematic interaction parameter α is changed. When α =2.5, we find that the first-order volume transition takes place at a critical temperature T_c in the isotropic phase above T°_{NI}. This first-order volume transition has been discussed for gels immersed in isotropic solvents [1] and corresponds to the isotropic–isotropic phase separation in the binary mixtures [19]. When the nematic interaction parameter α is increased, the critical temperature T_c decreases. For the larger values of α, the first-order volume transition disappears and we have only the second-order volume transition at the nematic-isotropic transition temperature T°_{NI} of the pure liquid crystal.

Figure 5 shows the predicted volume phase transition of the PS-gel immersed in the liquid crystal (EBBA). We used $n_r=1.5$ and $\alpha=5.35$. These parameters have been used for the comparison of the theoretical calculation

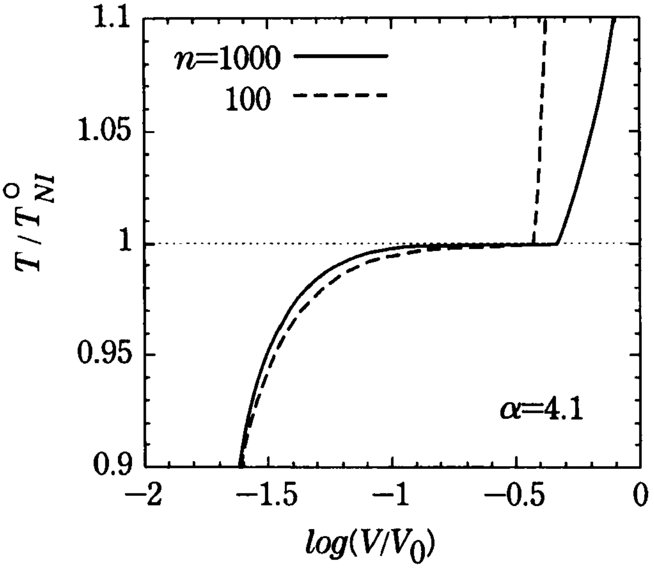

FIGURE 2 The swelling ratio V/V_0 of the gel plotted against the reduced temperature T/T_{NI}° for $n = 100$, 1000 with $\alpha = 4.1$.

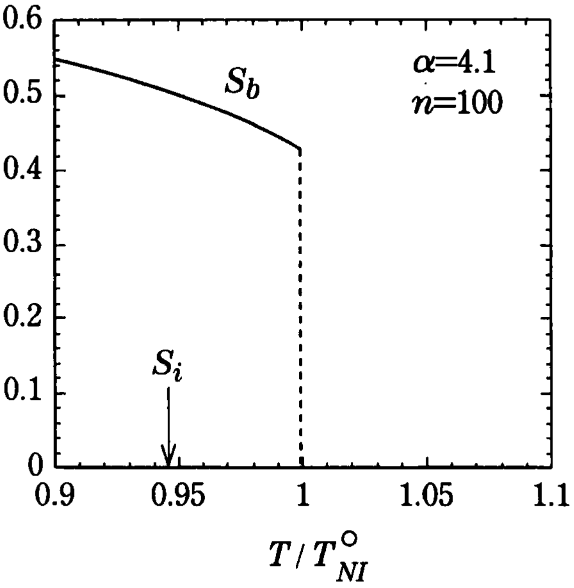

FIGURE 3 The orientational order parameter $S_i(S_b)$ of the liquid crystals existing inside (out side) of the gel plotted against the reduced temperature T/T_{NI}°.

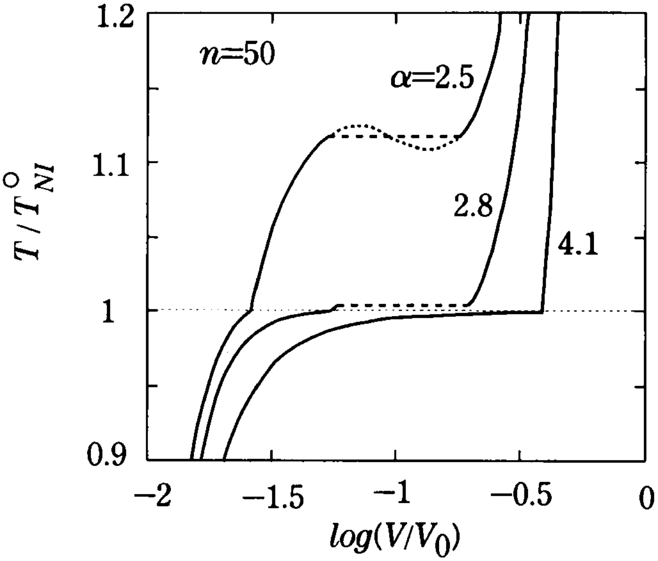

FIGURE 4 The swelling ratio of the gel for $n = 50$. The nematic interaction parameter α is changed.

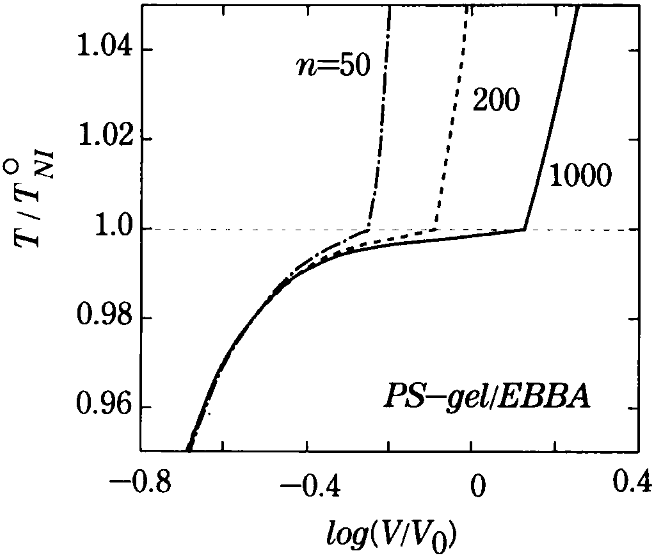

FIGURE 5 The predicted volume phase transition of the PS-gel dissolved in the liquid crystal (EBBA).

with the observed phase diagram in the binary mixture of PS and EBBA [19]. We also take $\phi_o = 0.07$ and n is changed. As temperature is decreased, the second-order volume phase transition occurs for all values of n. Below T°_{NI}, the gel collapses into a globule state and the volume of the condensed gel is almostly independent of n.

4. CONCLUSION

The gels immersed in liquid crystal solvents show the second order volume phase transition at the nematic-isotropic temperature T°_{NI} of the pure liquid crystals existing outside of the gel. Below T°_{NI}, the gel is condensed by the nematic ordering of the liquid crystal solvents. It is also of great interests to study critical phenomena of gels near T°_{NI} where the fluctuation of concentration and that of orientational order parameter of liquid crystals prevail. We also find the first-order volume transition in the isotropic phase above T°_{NI}. The experimental investigations of the volume phase transition of gels in liquid crystal solvents are desirable.

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