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Anisotropic Swelling and Phase Behavior of Monodomain Nematic Networks in Nematogenic Solvents

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ABSTRACT: Equilibrium swelling behavior of uniaxially oriented nematic networks in nematogenic solvents has been studied in the temperature (T) range covering the two independent nematic−isotropic transition temperatures for the swollen network (T_{NI}^{G}) and the surrounding solvent (T_{NI}^{S}; $T_{NI}^{G} > T_{NI}^{S}$). The swollen isotropic state smoothly changes into the shrunken nematic state with an elongation along the director axis within a narrow temperature range around T_{NI}^{G}. In the region of $T_{NI}^{S} < T < T_{NI}^{G}$, where the surrounding solvents are in the isotropic state, the shrunken nematic gels reswell with a further increase in shape anisotropy upon cooling. In the totally nematic phase of $T < T_{NI}^{S}$, the shape anisotropy increases without significant volume change with decreasing T. A mean field theory satisfactorily describes the features of experimental data, although a sharp transition predicted disagrees with the smooth transition observed. The polydomain nematic network without global director orientation shows no anisotropy in swelling but exhibits substantially the same T dependence of swelling degree as the corresponding monodomain system. A striking difference is that the polydomain system undergoes a discontinuous volume transition, unlike the continuous transition in the monodomain system.

Introduction

Nematic−isotropic (N−I) transition yields interesting phase behavior in the binary systems composed of liquid crystalline polymers and nematic solvents.[1−4] Nematic polymer networks swollen in isotropic[5,6] or nematic solvents[7,8] undergo a large volume change upon the N−I transition. The volume transition of nematic gels was first observed in polydomain systems.[7] Owing to the absence of global director orientation, the polydomain nematic gels exhibit no anisotropy in swelling. Our previous paper has demonstrated that the monodomain nematic networks with global director alignment swollen in isotropic solvents show a macroscopic elongation along the director axis as well as a significant volume reduction upon nematic ordering.[6]

In the present paper, we investigate the volume phase transition of the monodomain nematic networks in nematic solvents. This system has the two independent N−I transition temperatures, i.e., T_{NI}^{G} and T_{NI}^{S} for the swollen gel and the surrounding solvent, respectively. In the systems with $T_{NI}^{G} > T_{NI}^{S}$, the three characteristic temperature (T) regions appear: the totally isotropic phase ($T > T_{NI}^{G}$), the totally nematic phase ($T < T_{NI}^{S}$), and the phase inside the gel is nematic, whereas the phase of the surrounding solvent is isotropic ($T_{NI}^{S} < T < T_{NI}^{G}$). The equilibrium swelling degree of polydomain nematic networks shows the T dependence specific to each T region, resulting in the reentrant T dependence with a discontinuous change at T_{NI}^{G}.[7,8] Meanwhile, it still remains to be understood how the presence of global director orientation in nematic networks influences the shape anisotropy and swelling degree in nematic solvent systems. Yusuf et al.[9] reported the T dependence of the swelling degree of a monodomain nematic network in nematic solvents under a finite cooling rate. The cooling rate (0.7 °C/min) in their experiment was, however, presumably too first to achieve the swelling equilibrium at each T,[10] and thus their data are not sufficient to discuss the swelling and phase behavior from the thermodynamic viewpoint. In the present study, we have carefully equilibrated the swelling at each temperature and measured the equilibrium volume and dimensions in the directions parallel and perpendicular to the director. Further, we describe a theory for the equilibrium anisotropic swelling of nematic gels in nematic solvents. The experimental data are compared with the theoretical prediction.

Theory for Equilibrium Anisotropic Swelling of Nematic Networks in Nematic Solvents

In this section, we present the mean field theory for the equilibrium anisotropic swelling of uniaxially oriented nematic networks in nematogenic solvents. The present theory is based on the line of the earlier models[11,12] and is an extension of the model for nematic networks in nonmesomorphic solvents in our previous study.[6] The details of the theoretical assumptions and limitations were mentioned in ref 6.

We consider here the nematic networks composed of mesogenic and nonnematogenic (spacer) segments with the axial ratios of n_m and n_s, respectively. The number of the total segments between adjacent cross-links (n) is given by $n = (n_m + n_s)t$ where t is the number of repeating units. The volume fraction of network in the swollen state (ϕ) is expressed as

$$\phi = \frac{anN_g}{a(nN_g + n_0N_s)} \qquad (1)$$

where a, n_0, N_g, and N_s are the volume of an unit segment, the axial ratio of the nematic solvent, the numbers of the network chains, and the solvent molecules, respectively. The anisotropic swelling with uni-

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axial orientation is characterized by the principal ratios parallel and normal to the director (λ_L and λ_T, respectively) as

$$\phi^0/\phi = \lambda_L\lambda_T^{\,2} \qquad (2)$$

where the superscript 0 denotes the state of network formation.

The change of total free energy density (free energy per lattice site) Δf upon swelling is composed of the three terms:[11,12]

$$\Delta f = \Delta f_{\mathrm{el}} + \Delta f_{\mathrm{mix}} + \Delta f_{\mathrm{nem}} \qquad (3)$$

where f_{el}, f_{mix}, and f_{nem} are the free energy densities of network elasticity, isotropic mixing, and nematic ordering, respectively.

On the basis of the model of Warner et al.,[11,13,14] the expression of Δf_{el} for nematic networks was derived as a function of ϕ and the orientational order parameter of the chain backbone S_m:[6]

$$\frac{\Delta f_{\mathrm{el}}}{k_BT} = \frac{3\phi}{2n\phi^0}\left[\left(\frac{\phi^0}{\phi}\right)^{2/3}\left(\frac{A^0}{A}\right)^{1/3} - 1 - \frac{1}{3}\ln\left(\frac{A^0}{A}\right)\right] \qquad (4)$$

where k_B and T are the Boltzmann constant and absolute temperature, respectively, and

$$A = (1 + 2S_m)(1 - S_m)^2 \qquad (5a)$$

$$A^0 = (1 + 2S_m^{\,0})(1 - S_m^{\,0})^2 \qquad (5b)$$

The spontaneous uniaxial elongation λ_L is obtained by taking $(\partial\Delta f/\partial\lambda_L)_{\phi,S} = (\partial\Delta f_{\mathrm{el}}/\partial\lambda_L)_{\phi,S} = 0$ because λ_L only appears in f_{el}:

$$\lambda_L = \left(\frac{\phi^0}{\phi}\right)^{1/3}\left(\frac{1 + 2S_m}{1 - S_m}\right)^{1/3}\left(\frac{1 - S_m^{\,0}}{1 + 2S_m^{\,0}}\right)^{1/3} \qquad (6)$$

The reference state for λ_L ($\lambda_L = 1$) is the state of network formation, i.e., the nematic phase with ϕ^0 and S_m^0. For the experimental convenience, each of λ_L and λ_T is rescaled as $\lambda_\parallel$ and $\lambda_\perp$, whose reference state is the dry isotropic state with $\phi = 1$ and $S_m = 0$, respectively:

$$\lambda_\parallel = \frac{\lambda_L}{\lambda_L^{\,0}} = \frac{1}{\phi^{1/3}}\left(\frac{1 + 2S_m}{1 - S_m}\right)^{1/3} \qquad (7a)$$

and

$$\lambda_\perp = \frac{\lambda_T}{\lambda_T^{\,0}} = \frac{1}{\phi^{1/3}}\left(\frac{1 - S_m}{1 + 2S_m}\right)^{1/6} \qquad (7b)$$

where $\lambda_L^0 = [\phi^0(1 - S_m^0)/(1 + 2S_m^0)]^{1/3}$ in the dry isotropic state is employed. The corresponding swelling degree Q is given by

$$Q = \frac{1}{\phi} = \lambda_\parallel\lambda_\perp^{\,2} \qquad (8)$$

The ratio $\alpha = \lambda_\parallel/\lambda_\perp$ is a measure for shape anisotropy of swollen networks:

$$\alpha = \lambda_\parallel/\lambda_\perp = \left(\frac{1 + 2S_m}{1 - S_m}\right)^{1/2} \qquad (9)$$

The principal ratios ($\lambda_\parallel$, $\lambda_\perp$), swelling degree (Q), and shape anisotropy (α), defined by eqs 7–9, are independent of the state of network formation (S_m^0 and ϕ^0), and they only depend on the state of interest (S_m and ϕ).

The term Δf_{mix} may be written within the Flory–Huggins model as[12,15]

$$\frac{\Delta f_{\mathrm{mix}}}{k_BT} = \frac{(1 - \phi)}{n_0}\ln(1 - \phi) + \chi\phi_S(1 - \phi_S) \qquad (10)$$

where χ represents the Flory–Huggins parameter for the mixing interaction between the non-nematogenic (spacer) segments and the nematic molecules (mesogens on network and nematic solvents), and ϕ_s is the volume fraction of spacer given by $\phi_s = \phi n_s/(n_m + n_s)$. For simplicity, the nematic solvent is assumed to act as an athermal solvent for the mesogens.

According to the generalized Maier–Saupe theory for binary nematic mixtures,[16,17] Δf_{nem} may be written as

$$\frac{\Delta f_{\mathrm{nem}}}{k_BT} = \sum_{i=\mathrm{m},0}\frac{\phi_i}{n_i}\int \psi(\theta_i)\ln[4\pi\psi(\theta_i)]\,\mathrm{d}\Omega_i - \frac{1}{2}\nu_{\mathrm{mm}}\phi_m^{\,2}S_m^{\,2} - \frac{1}{2}\nu_{00}(1 - \phi)^2S_0^{\,2} - \nu_{\mathrm{m}0}\phi_m(1 - \phi)S_mS_0 \qquad (11)$$

where the subscripts m and 0 stand for the mesogen on the network and the solvent inside the gel, respectively, and ϕ_m is the volume fraction of mesogen given by $\phi_m = \phi\, n_m/(n_m + n_s) = \phi(1 - p)$ with the spacer fraction $p = n_s/(n_m + n_s)$. ψ is the orientation distribution function, θ_i (i = m,0) denotes the angle between the director and the corresponding molecule, and Ω_i is the solid angle. We assume here that the order parameter for the mesogens is equivalent to that for the chain backbone (S_m) for simplicity. The Maier–Saupe interaction parameters ν_{mm}, ν_{00}, and $\nu_{\mathrm{m}0}$ characterize the nematic interaction between the two nematic molecules of interest. They are assumed to be proportional to reciprocal temperature, and in particular, ν_{00} is correlated with the N–I transition temperature of the solvent ($T_{NI}^{\,S}$) as $\nu_{00} = 4.54\ T_{NI}^{\,S}/(n_0T)$.[18] The cross-interaction $\nu_{\mathrm{m}0}$ is conventionally related to ν_{mm} and ν_{00} as $\nu_{\mathrm{m}0} = \kappa\,(\nu_{\mathrm{m}0}\,\nu_{00})^{1/2}$ using a proportional constant κ representing the strength of the cross-interaction.[19] The orientation distribution function $\psi(\theta_i)$ for each nematic molecule is related with the corresponding order parameter S_i ($\boldsymbol{i}$ = m,0) as

$$S_{\mathrm{i}} = \int \frac{1}{2}(3\cos^2\theta_i - 1)\psi(\theta_i)\,\mathrm{d}\Omega_i \qquad (12)$$

The function $\psi(\theta_i)$ (i = m,0) is expressed by

$$\psi(\theta_i) = \frac{1}{Z_i}\exp\left[\frac{1}{2}\eta_i(3\cos^2\theta_i - 1)\right] \qquad (13)$$

where $Z_i = \int \exp[\eta_i(3\cos^2\theta_i - 1)/2]\,\mathrm{d}\Omega_i$ is the partition function to normalize $\psi(\theta_i)$, and η_i is a dimensionless parameter, characterizing the strength of the nematic field. The expression of η_i (i = m,0) as a function of S_m,

S_0, and ϕ is obtained by taking $\partial\Delta f/\partial\psi(\theta_i) = 0$:

$$\eta_m = n_m[\nu_{mm}\phi_m S_m + \nu_{m0}(1-\phi)S_0] - \frac{3n_m S_m(1-S_m)}{n\phi_m A}\left[\left(\frac{\phi A^0}{\phi^0 A}\right)^{1/3} - \frac{\phi}{\phi^0}\right] \tag{14}$$

$$\eta_0 = n_0[\nu_{m0}\phi_m S_m + \nu_{00}(1-\phi)S_0] \tag{15}$$

The order parameter S_b for the surrounding solvent is given by eqs 12 and 13 with $i = b$ and

$$\eta_b = n_0\, \nu_{00}\, S_b \tag{16}$$

In the swelling equilibrium, the chemical potential of the solvent inside the gel ($\mu = f - \phi\partial f/\partial\phi$) is balanced with that of the solvent outside the gel ($\mu°$):

$$\mu(\phi, S_m, S_0) = \mu^0\,(S_b) \tag{17}$$

Equation 17 yields the condition for equilibrium swelling:

$$\frac{1}{n}\left(\frac{\phi A^0}{\phi^0 A}\right)^{1/3} + \frac{\ln(1-\phi)}{n_0} + \frac{\phi}{n_0} + \chi\phi_s^{\,2} + \frac{1}{2}\nu_{mm}S_m^{\,2}\phi_m^{\,2} + \nu_{m0}S_m S_0\phi_m(1-\phi) + \frac{1}{2}\nu_{00}[S_0^{\,2}(1-\phi)^2 - S_b^{\,2}] + \frac{1}{n_0}\ln\frac{Z_b}{Z_0} = 0 \tag{18}$$

The equilibrium values of ϕ (or Q) and S_i (i = m,0,b) as a function of T are obtained as the solutions satisfying eqs 12 and 18. The corresponding principal ratios $\lambda_{\parallel}$ and $\lambda_{\perp}$ are calculated with eq 7.

Experimental Section

Sample Preparation. The side chain monodomain nematic networks with uniaxial orientation were prepared by the same method as in the previous study.[6] The molecular structure of the employed acrylate mesogen A-6OCB is illustrated in Figure 1. The cross-linker (1,6-hexanediol diacrylate) concentration was 7 mol % in the feed. The reactants, including the photoinitiator (Irgacure 784), were photopolymerized between the glass plates coated with the unidirectionally rubbed polyimide layer. The cell gap was 25 μm. The resulting gel films were carefully separated from the cells and allowed to swell in dichloromethane to wash out the unreacted materials. The dry monodomain nematic networks MONO-LCN were obtained by deswelling and drying the swollen networks. The N−I transition temperature of the dry networks is 107 °C. The uniform birefringence resulting from uniaxial orientation was observed in the nematic phase by cross-polarizing microscopy.

The polydomain nematic network POLY-LCN without global director orientation was prepared in the same manner as MONO-LCN but using the glass plates without rubbed polymer layers. The mesogenic monomers were cross-linked in the polydomain nematic state. The N−I transition temperature of POLY-LCN in the dry state is 128 °C.

Swelling Measurement. The small specimens with an area of ca. 0.5 mm × 0.5 mm cut out from the dry network film were used for swelling experiments to shorten the time required for equilibration. The networks were immersed in the low-molecular-mass nematic liquid crystal, 4-*n*-pentyl-4′-cyanobiphenyl (5CB) or 4-*n*-heptylbenzoic acid 4-cyanophenyl ester (7CPB), with the N−I transition temperatures of 35.0 or 54.2 °C, respectively. They have a quoted purity of at least 99% (Sigma-Aldrich) and were used as received without further purification. The chemical structures are shown in Figure 1. The measurements of the dimensions of the gel and the phase observation were carried out on a polarizing optical microscope Nikon E600POL equipped with a Linkam LK-600PM sample stage under a nitrogen atmosphere. The initial swelling temperature was 65 or 78 °C in the 5CB or 7CPB systems, respectively, where the systems were totally in the isotropic phase. The dimensions (d) of the gel at each temperature were measured after confirming the swelling equilibrium. The swelling temperature was stepwise decreased. The equilibrium swelling behavior in the heating process was also investigated after the measurements in the cooling process. The principal ratio λ in the swollen state is obtained as

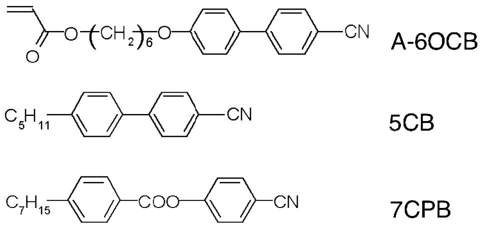

Figure 1. Molecular structures of the employed mesogenic monomer and solvents.

$$\lambda_{\parallel} = d_{\parallel}/d_{\parallel,\mathrm{dry}}^{\ \ I} \tag{19a}$$

$$\lambda_{\perp} = d_{\perp}/d_{\perp,\mathrm{dry}}^{\ \ I} \tag{19b}$$

where the subscripts ∥ and ⊥ denote the director direction and its perpendicular direction, respectively, and the superscript I stands for the isotropic state. The changes of $d_{\parallel,\mathrm{dry}}^{\ \ I}$ and $d_{\perp,\mathrm{dry}}^{\ \ I}$ in response to temperature variation were negligibly small (less than 1%). The equilibrium degree of swelling Q is calculated by

$$Q = \lambda_{\parallel}\lambda_{\perp}^{\,2} \tag{20}$$

where we assume uniaxial orientation, although the presence of cell walls upon cross-linking may yield a slight deviation. In the swelling measurements for POLY-LCN without global director alignment, the two orthogonal directions were arbitrarily chosen as the principal axes.

Results and Discussion

Equilibrium Swelling of Monodomain Nematic Networks in Nematic Solvents. Part a of Figures 2 and 3 displays Q, $\lambda_{\parallel}$ and $\lambda_{\perp}$ as a function of temperature (T) for MONO-LCN in 5CB and 7CPB, respectively. Part b of Figures 2 and 3 displays the T dependence of the degree of shape anisotropy α (= $\lambda_{\parallel}/\lambda_{\perp}$). As can be seen in the figures, the two systems exhibit qualitatively the same features for the swelling and phase behavior. The three characteristic T regions are present because of the two independent N−I transition temperatures $T_{NI}^{\ G}$ and $T_{NI}^{\ S}$ inside and outside the gel, respectively: the totally isotropic phase $T > T_{NI}^{\ G}$, the totally nematic phase $T < T_{NI}^{\ S}$, and the phase inside the gel is nematic, whereas that outside the gel is isotropic $T_{NI}^{\ S} < T < T_{NI}^{\ G}$. In the region of $T < T_{NI}^{\ G}$, the nematic network and the solvent inside the gel form a single monodomain nematic phase. The optical micrographs in Figure 4 show the formation of the monodomain nematic phase with uniaxial orientation. The 7CPB system has a higher $T_{NI}^{\ G}$ than that of the 5CB system. As shown before,[8,20,21] $T_{NI}^{\ G}$ is qualitatively interpreted as the N−I transition temperature for a miscible binary mixture of the nematic network and nematic solvent with a certain composition. The higher $T_{NI}^{\ G}$ of the 7CPB system is simply attributable to the higher $T_{NI}^{\ S}$ because the values of Q around $T_{NI}^{\ G}$ for the two systems are comparable.

It can be seen in Figure 2 that the volume change accompanied by the shape variation is thermoreversible.

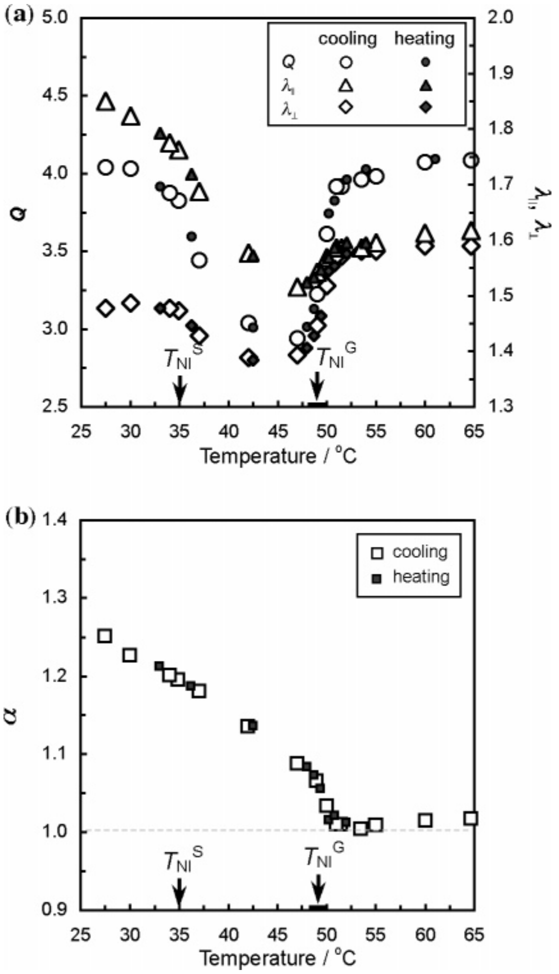

Figure 2. (a) The equilibrium swelling degree (Q) and principal ratios in the directions parallel and perpendicular to the director ($\lambda_\parallel$ and $\lambda_\perp$, respectively) as a function of temperature for MONO-LCN in 5CB with $T_{NI}^S = 35.0$ °C. The gel exhibits a smooth phase transition between the isotropic swollen and nematic shrunken states around 48 °C (T_{NI}^G) with a shape variation. There is no significant difference in the swelling and phase behavior between the heating and cooling processes. (b) The temperature dependence of the degree of shape anisotropy $\alpha = \lambda_\parallel/\lambda_\perp$.

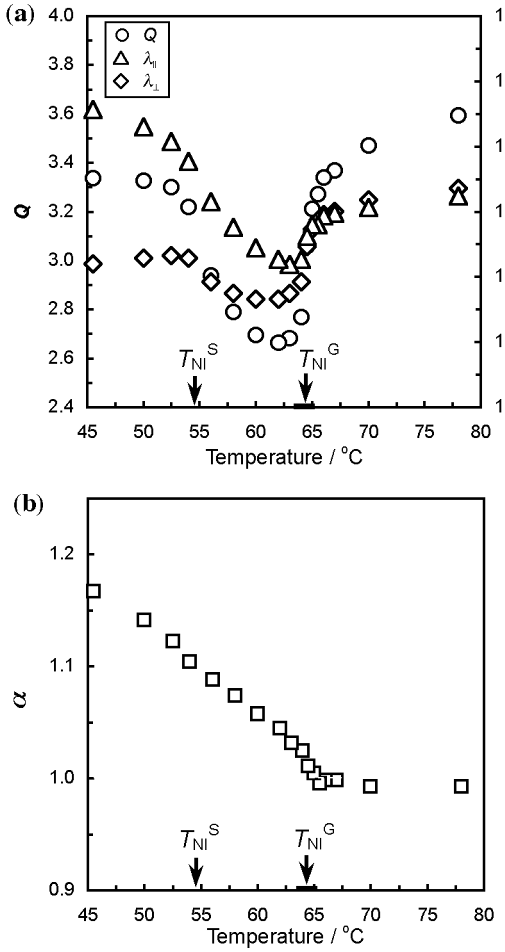

Figure 3. (a) The equilibrium swelling degree (Q) and principal ratios in the directions parallel and perpendicular to the director ($\lambda_\parallel$ and $\lambda_\perp$, respectively) as a function of temperature for MONO-LCN in 7CPB with $T_{NI}^S = 54.2$ °C. The gel exhibits a smooth phase transition between the isotropic swollen and nematic shrunken states around 64 °C (T_{NI}^G) with a shape variation. (b) The temperature dependence of the degree of shape anisotropy $\alpha = \lambda_\parallel/\lambda_\perp$.

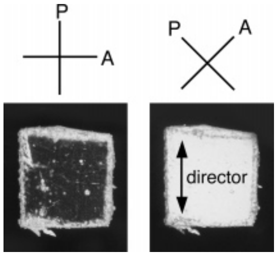

Figure 4. Optical micrographs of MONO-LCN swollen in 5CB at 47 °C. The arrow A or P denotes the optical axis of the analyzer or polarizer, respectively. The pictures show the formation of monodomain nematic phase with uniaxial orientation inside the gel. The surrounding solvent is in the isotropic phase. The incomplete dark regions along the outline of the gel (left picture) stem from the birefringence of the scratches formed unavoidably when cutting out the specimen from the dry network film.

The T dependence of anisotropic swelling observed in the two systems is schematically shown in Figure 5. In the totally isotropic phase, the gel swells largely and exhibits no shape anisotropy ($\alpha = 1$). Upon cooling to T_{NI}^G (around 49 °C or 64 °C for 5CB and 7CPB systems, respectively), the swollen isotropic gel is smoothly transformed into the shrunken monodomain nematic gel without discontinuity in volume. The discussion about the continuous transition will be given later. Of importance is that a shape change takes place simultaneously with the volume reduction at T_{NI}^G. In the nematic phase, the gel has a shape elongated in the director direction ($\alpha > 1$). When the system is further cooled, Q of the nematic gel increases again together with a further increase in shape anisotropy (α). At temperatures around T_{NI}^S, Q of the nematic gel becomes almost identical with that of the isotropic gel at $T > T_{NI}^G$. The nematic ordering of the surrounding solvent occurs at T_{NI}^S, which yields an inflection in the swelling curve without discontinuity. The comparison of the T dependence of Q and λ in the regions of $T < T_{NI}^S$ and $T_{NI}^S < T < T_{NI}^G$ reveals the effects of nematic order of the surrounding solvent on swelling: Q is strongly T dependent in the regime above T_{NI}^S, whereas Q in the region below T_{NI}^S is almost T independent; upon cooling, both $\lambda_\parallel$ and $\lambda_\perp$ increase at temperatures above T_{NI}^S, whereas in the region below T_{NI}^S, $\lambda_\parallel$ increases but $\lambda_\perp$ slightly decreases. This shows that when the surrounding solvent is in the nematic phase, the shape anisotropy grows without significant volume change upon cooling.

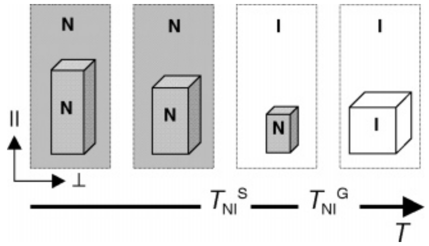

Figure 5. Schematics for the temperature dependence of anisotropic swelling of uniaxially oriented nematic networks in nematic solvents. At T_{NI}^G, the gel undergoes a phase transition between the isotropic swollen state and the nematic shrunken state with a shape stretched along the director axis (||). In the region of $T_{NI}^S < T < T_{NI}^G$, where the surrounding solvent is in the isotropic state, both volume and shape anisotropy of the nematic gel increase upon cooling. The anisotropically swollen nematic gel at $T < T_{NI}^S$ has almost the same volume as the isotropic gel at $T > T_{NI}^G$. In the totally nematic phase of $T < T_{NI}^S$, the swelling degree is almost T independent, whereas the shape anisotropy grows upon cooling. The dimensional and volume changes in the figure is amplified for explanation.

A role of nematic order in swelling is also recognizable by comparing the isotropic gel at $T > T_{NI}^G$ and the nematic gel at $T < T_{NI}^S$. The two gels have almost the same volume (Q) but they differ in shape (α). This comparison shows that when the phases of nematic molecules inside and outside the gel are identical, whether the phase of interest is isotropic or nematic has no appreciable influence on swelling degree (gel volume), whereas it significantly affects the shape of gel. This point will also be discussed from the theoretical viewpoint in the later section.

Comparison of Volume Phase Transitions of Monodomain and Polydomain Nematic Networks. Figure 6 displays the T dependence of Q, λ, and α for POLY-LCN in 7CPB. The result is qualitatively similar to those for polydomain nematic gels in nematic solvents reported before.[7,8] POLY-LCN exhibits no anisotropy in swelling (α = 1) within experimental error because of the absence of global director orientation. Of significance is that POLY-LCN is similar in the reentrant T dependence of Q to MONO-LCN, apart from a difference in the volume transition behavior at T_{NI}^G. This similarity indicates that the T dependence of gel volume is governed by local director orientation of nematic molecules, and it is almost unaffected by the presence of global director orientation. A typical size of an individual domain in polydomain structures is on the order of a micrometer,[22,23] far larger than network meshes. Each constituent nematic domain is expected to swell anisotropically in the same way as the corresponding monodomain system does. In consequence, the swelling degree of polydomain systems show almost the same T dependence as that of monodomain systems, although the swelling of the polydomain networks is macroscopically isotropic because of the global cancellation of the local shape anisotropy by the random director orientation. It is surprising that the interaction between the topologically connected domains with different director directions in polydomain systems apparently has no significant influence on the T dependence of Q. Such interaction may also be globally canceled out because of the random orientation.

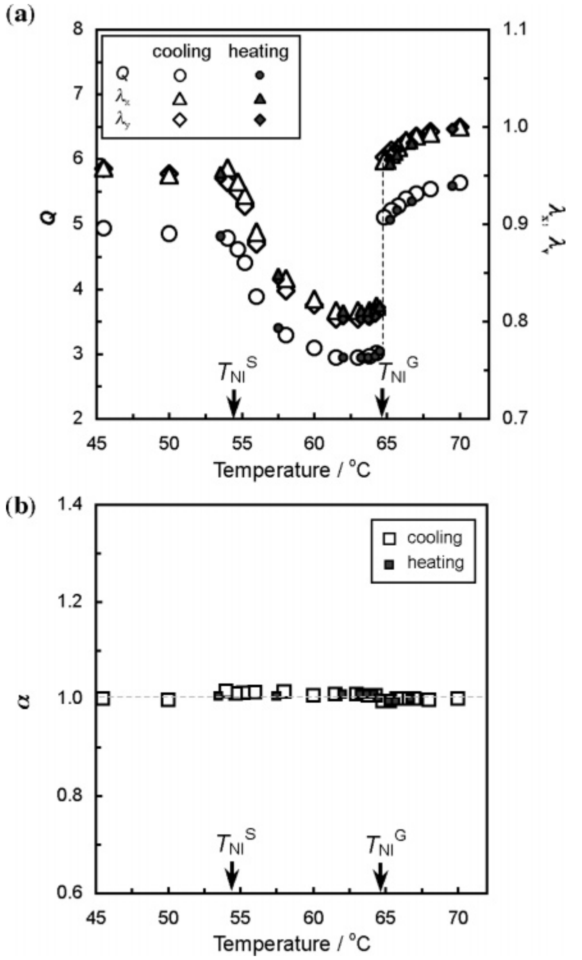

Figure 6. (a) The equilibrium swelling degree (Q) and principal ratios (λ_x and λ_y) as a function of temperature for POLY-LCN in 7CPB with $T_{NI}^S = 54.2$ °C. The gel exhibits a discontinuous transition between the isotropic swollen and nematic shrunken states at 64.8 °C (T_{NI}^G). The gel shows no anisotropy in swelling ($\lambda_x = \lambda_y$). There is no significant difference in the swelling and phase behavior between the heating and cooling processes. (b) The temperature dependence of the degree of shape anisotropy $\alpha = \lambda_x/\lambda_y$. α is almost unity because of isotropic swelling.

Almost the same T_{NI}^G (≈65 °C) of MONO-LCN and POLY-LCN is fortuitous because the N−I transition temperatures in the dry state (T_{NI}^N) as well as Q around T_{NI}^G for the two networks are different. As shown in the previous papers,[8,20,21] T_{NI}^G is roughly approximated by a simple additivity with T_{NI}^N, T_{NI}^S, and the volume fraction of network around T_{NI}^G in the isotropic phase (ϕ_{NI}): $T_{NI}^G = (1 - \phi_{NI})\, T_{NI}^S + \phi_{NI}\, T_{NI}^N$. This approximation yields the close values of T_{NI}^G for MONO-LCN and POLY-LCN (71 and 69 °C, respectively). It will be difficult to discuss the effect purely stemming from the difference between monodomain and polydomain structures on the magnitudes of Q and T_{NI}^G. Amount of cross-link strongly influences T_{NI}^N and Q.[20] The different orientational states of mesogens during synthesis are expected to affect the effective cross-linking densities, even if the amounts of cross-linker in the feed are identical. The temperature T_{NI}^N of POLY-LCN is unexpectedly rather higher than that of MONO-LCN, which is due to the difference in the effective cross-linking density. In the case of polydomain nematic networks, T_{NI}^N decreases with increasing the amount of cross-linker in the feed.[20] The effective cross-linking density of POLY-LCN is presumably lower than that of MONO-LCN.

A striking difference is that the volume phase transition of POLY-LCN takes place discontinuously, unlike that of MONO-LCN, occurring smoothly without dis-

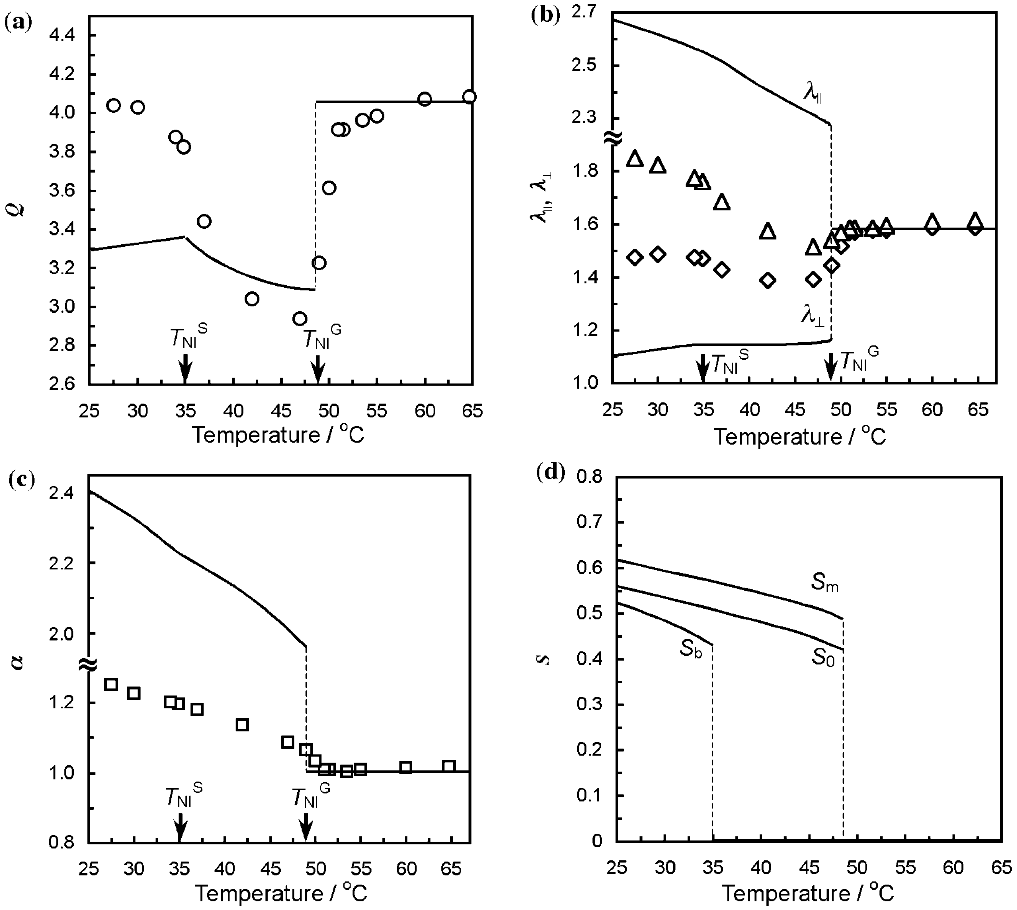

Figure 7. Comparison of the theoretical prediction with the data of MONO-LCN in 5CB for (a) equilibrium swelling degree (Q); (b) equilibrium principal ratios in the directions parallel and perpendicular to the director ($\lambda_\parallel$ and $\lambda_\perp$, respectively); (c) shape anisotropy $\alpha = \lambda_\parallel/\lambda_\perp$. (d) The theoretical order parameters S_m, S_0 and S_b calculated simultaneously with Q as a function of T. The values of parameters used for the data-fitting are $\phi^0 = 0.5$, $S_m^0 = 0.5$, $n_0 = 2.9$, $n = 50$, $n_m = 3.1$, $p = 0.15$, $\nu_{00}/\chi = 1000$, $\nu_{mm}/\nu_{00} = 1.3$, $\kappa = 0.998$. The lines represent the predictions of the theory yielding a sharp N−I transition.

continuity. The similar difference is observed in the isotropic solvent systems.[6] The continuous transition in the swollen MONO-LCN is apparently analogous to the smooth transitions of the orientational order parameter and the shape in dry monodomain nematic networks reported by many researchers.[24−28] The origin of the smooth transition without the expected discontinuity is left unsettled. There are two possible explanations. The first is that the discontinuity vanishes because of the internal stress beyond a critical value, such as a liquid−gas transition under high pressures.[29] The second attributes the broadening of the transition to heterogeneity in network structures or local nematic order, yielding a finite distribution of N−I transition temperatures.[28,30] To the author's knowledge, a volume transition of swollen polydomain nematic networks is only an example of the transition with a first-order discontinuity in nematic network systems. The discontinuity seen in swollen polydomain systems is lost in swollen monodomain systems, which should be an important clue to elucidate the origin of the smooth transition. It is likely that this can be explained by either of the two explanations. In the first explanation, the internal stress to induce the disappearance of discontinuity might originate from an external field to achieve the global alignment of mesogens upon cross-linking. Such internal stress is absent in the formation of polydomain systems. The second explanation is based on heterogeneity in local nematic order. The heterogeneity could form upon cross-linking in the monodomain state made artificially and exceed a critical size (ξ) below which a sharp transition occurs. In the polydomain systems made in a real thermodynamic equilibrium state without external field, such type of heterogeneity does not form. The size of the individual domain (on the order of a micrometer[22,23]) in polydomain systems would be smaller than ξ, which explains a sharp transition in polydomain systems.

Comparison of Experimental Data with Theoretical Predictions. Figure 7 illustrates the comparison of the experimental data for MONO-LCN in 7CPB with the theoretical prediction. Parts a, b, and c of the figure depict the results for Q, λ, and α, respectively. Part d shows the corresponding-to-theoretical orientational order parameters S_m , S_0, and S_b as a function of T. The present theory predicts a discontinuous change in each quantity at T_{NI}^G. The theory satisfactorily describes the features of the reentrant T dependence of Q with a shape variation in the experiment, although it yields an overestimation of the shape anisotropy and an underestimation of Q in the totally nematic phase. The theory demonstrates that the swelling degree and the shape anisotropy are mainly governed by the order parameters of the constituent nematic molecules. The simultaneous jumps in S_m and S_0 (the formation of a single nematic phase) from zero to finite values at T_{NI}^G give rise to a transition from the swollen state into the shrunken state with an elongation along the director. Upon cooling in the region of $T_{NI}^S < T < T_{NI}^G$ (where $S_b = 0$), the increases in S_m and S_0 thermodynamically drive the reswelling together with a further increase in shape anisotropy. A jump of S_b at T_{NI}^S (the nematic ordering of the surrounding solvent) yields a kink in the $\lambda-T$ and $Q-T$ curves without discontinuity. When temperatures decrease in the totally nematic phase, the growths of S_m, S_0, and S_b further enhance the shape anisotropy without appreciable change in Q. Meanwhile, the presence of nematic order in the surrounding solvent weakens the T dependence of $\lambda_{\parallel}$ and yields a slightly positive T dependence of $\lambda_{\perp}$. The swelling degree is almost independent of T in the totally isotropic and nematic phases, in both of which there exists no significant difference in the orientational orders inside and outside the gel: $S_m = S_0 = S_b = 0$ at $T > T_{NI}^G$; $S_m \approx S_0 \approx S_b$ at $T < T_{NI}^S$. The swelling degree is strongly T dependent in the regime of $T_{NI}^S < T < T_{NI}^G$, where the orientational orders inside the gel are present and that outside the gel is absent.

To improve the underestimation of Q at $T < T_{NI}^S$, inappropriate values of κ (>1) for the present systems are needed. The condition $\kappa > 1$ corresponds to the case of unusually strong cross-nematic interaction, where the interaction between the dissimilar nematogens is stronger than that between the same nematogens.[19] The underestimation of Q in the totally nematic phase is a point to be improved in the present theory.

The most probable reason for the excessive shape anisotropy in the theory is the overestimation of S_m (>0.5) by the mean field approach. As seen in eq 9, α increases with increasing S_m. The maximum value of S_m for a similar acrylate-based side chain nematic network was reported to be about 0.3 in the dry state.[27] On the basis of eq 9, the value of S_m corresponding to the maximum of α (= 1.25) in the present experiment is estimated to be ca. 0.2, rather smaller than S_m calculated from the mean field approach.

Summary

The equilibrium anisotropic swelling behavior of monodomain nematic networks in nematic solvents with $T_{NI}^G > T_{NI}^S$ has been studied. When the system in the totally isotropic phase ($T > T_{NI}^G$) is cooled to temperatures around T_{NI}^G, the swollen isotropic network is smoothly transformed into the shrunken monodomain nematic network with an elongation along the director axis (i.e., $\lambda_{\parallel} > \lambda_{\perp}$). Upon further cooling, the nematic gel surrounded by the solvent in the isotropic state swells again with accompanying the growths of $\lambda_{\parallel}$, $\lambda_{\perp}$, and the shape anisotropy ($\lambda_{\parallel}/\lambda_{\perp}$). The nematic ordering of the surrounding solvent at T_{NI}^S gives rise to a kink in the $Q-T$ and $\lambda-T$ curves without discontinuity. The volume of the gel in the totally nematic phase ($T < T_{NI}^S$) is comparable to that in the totally isotropic phase. At $T < T_{NI}^S$, the shape anisotropy increases without significant volume change upon cooling.

A mean field theory is successful in describing the main features of the experimental data, and it demonstrates that the T dependence of gel volume and shape anisotropy is mainly governed by the orientation degrees of the constituent nematic molecules.

The polydomain nematic networks without global director orientation exhibit no anisotropy in swelling but show almost the same T dependence of Q as that of the monodomain nematic networks. This suggests that the local orientational order within each constituent domain plays a major role in the T dependence of gel volume. Of significance is that the polydomain systems undergo a discontinuous volume transition at T_{NI}^G, unlike the smooth volume transition in the monodomain systems. This may be an important key to clarify the origin of the smooth transition of monodomain systems.

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Nomenclature

a = volume of a unit segment
n_i (i = 0, m, s) = axial ratio of molecule i (0: solvent molecule; m: mesogenic segment on network; s: spacer segment on network)
p = spacer fraction in network
n = number of total segments between adjacent cross-links
ϕ = volume fraction of network
ϕ^0 = volume fraction of network in the state of network formation
ϕ_i (i = m, s) = volume fraction of component i
N_g = number of network strands
N_s = number of solvent molecules inside gels
λ_L = principal ratio along the director measured from the state of network formation
λ_T = principal ratio normal to the director measured from the state of network formation
$\lambda_{\parallel}$ = principal ratio along the director measured from the dry isotropic state
$\lambda_{\perp}$ = principal ratio normal to the director measured from the dry isotropic state
S_i (i = m, 0, b) = orientational order parameter of component i (m: mesogen on network; 0: solvent inside gel; b: solvent outside gel)
Q = degree of swelling measured from the dry isotropic state
α = a measure of shape anisotropy
χ = Flory−Huggins parameter for the mixing interaction between nonmesomorphic segments and nematic molecules
ν_{ij} (i,j = m, 0) = Maier−Saupe interaction parameter for the nematic interaction between the molecules i and j
κ = constant representing the strength of cross nematic interaction
θ_i (i = m, 0, b) = angle between the director and molecule i
ψ_i (i = m, 0, b) = orientation distribution function for molecule i
Z_i (i = m, 0, b) = normalization factor for ψ_i
η_i (i = m, 0, b) = nematic field strength for molecule i

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(10) In the present study, at least 1 h was needed to achieve the swelling equilibrium at each temperature for the gel film of several tens of micrometers thickness. The samples with the thickness of over 100 μm in ref 9 will require a longer time for the swelling equilibrium. The swelling data in ref 9 obtained with a finite cooling rate will involve a large nonequilibrium effect. As a typical example, in ref 9, a swollen polydomain nematic network exhibited a continuous volume change at T_{NI}^{G}, which misses a discontinuity because of the nonequilibrium effect. In the equilibrium state, the polydomain systems undergo a discontinuous volume transition, as shown in ref 8 and Figure 6 in the present paper.

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