Volume transition of nematic gels in nematogenic solvents

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Equilibrium swelling and phase behavior of liquid crystalline (LC) networks swollen in miscible nematogenic solvents has been investigated by polarizing microscopy as a function of temperature. Four systems, i.e., each of two different LC networks comprising dissimilar mesogens in two different nematic solvents, exhibit essentially the same swelling and phase characteristics. The swelling characteristics strongly correlate with the phases of the LC molecules inside and outside the gel. The two independent nematic-isotropic transition temperatures for the gel (T_{NI}^G) and the surrounding pure solvent (T_{NI}^S; $T_{NI}^G > T_{NI}^S$ for all the systems examined) yield three characteristic temperature regions. In the totally isotropic and nematic phases ($T > T_{NI}^G$ and $T < T_{NI}^S$, respectively), the degree of equilibrium swelling (Q) is almost independent of T, and the magnitudes of Q in these phases are comparable. Meanwhile, Q strongly depends on T in the region $T_{NI}^S < T < T_{NI}^G$ where the LC phases inside and outside the gel are different, i.e., nematic and isotropic, respectively. Upon cooling down to T_{NI}^G from the totally isotropic phase, the nematic network and the miscible nematic solvent inside the gel form a single nematic phase, which causes a discontinuous decrease in gel volume: The swollen isotropic gel is discontinuously transformed into the shrunken nematic gel. As temperature decreases further, Q of the shrunken nematic gel surrounded by the isotropic LC solvent increases again, and Q at $T \approx T_{NI}^S$ reaches almost the same magnitude as that in the totally isotropic phase. The nematic ordering of the surrounding pure solvent takes place at T_{NI}^S, which yields an inflection of the Q-T curve without discontinuity. A mean field theory for nematic gel successfully describes the swelling and phase behavior observed. The theory also demonstrates that the nematic-isotropic transition of gel drives a volume transition; an increase in nematic order inside gel induces a further swelling of nematic gel surrounded by isotropic LC solvent. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1535896]

I. INTRODUCTION

Volume phase transition phenomena of polymer gels have been extensively investigated over the last 20 years. It has been reported that an infinitesimal change in an environmental intensive variable such as solvent composition,[1–3] pH,[4,5] and temperature[6–10] yields a discontinuous volume change for some polymer gels. These volume transitions are driven by the balance between the repulsive and attractive forces acting on the network chains such as van der Waals, hydrophobic, ionic, hydrogen bonding.[7,11] In previous communication,[12] we reported the first observation of the volume transition for liquid crystalline (LC) gels in a nematic solvent at the nematic-isotropic transition temperature of the gels (T_{NI}^G). This volume transition is triggered by nematic ordering of LC molecules inside the gel. This finding adds a new driving molecular force for volume transition phenomena. "Temperature-sensitive gels" exhibiting volume transition at a certain temperature have attracted much attention of scientist and technologists because of their applications to drug delivery systems and sensors, etc.[13–15] So far N-isopropylacrylamide-based gels have been known as a typical temperature-sensitive gel. LC gels undergoing a sharp and large volume change accompanied by nematic-isotropic

transition at T_{NI}^G is a new type of temperature-sensitive gel, which will extend the potential application of polymer gels to industrial device. LC networks swollen in LC solvent have also been expected as a soft actuator driven under electric field utilizing the anisotropic character that the orientation of mesogen is controllable by external field.[16–18] Elucidation of the correlation between swelling and phase behavior will provide the basis to develop further the applications of LC gels.

In a previous communication,[12] we also reported that the shrunken namatic gel swelled again with decreasing in temperature in the region $T_{NI}^S < T < T_{NI}^G$ where T_{NI}^S is the nematic-isotropic transition temperature of the surrounding pure LC solvent. The interesting swelling characteristics such as volume transition and reswelling behavior were observed in the nematic networks swollen in a dissimilar nematogen. In the present study, the swelling behavior of four systems, i.e., each of two different LC networks comprising dissimilar mesogens in two different nematic solvents, is investigated to confirm the universality of the nematic ordering induced-volume transition as well as the reentrant swelling behavior. A nematic network swollen in a similar nematogen is also examined to clarify if the dissimilarity between mesogen on network and nematic solvent is responsible for the characteristic swelling behavior. It is also interesting to survey how T_{NI}^G of swollen LC network depends on each of

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transition temperatures of solvent-free (dry) LC network ($T_{NI}^{G}*$) and nematic solvent (T_{NI}^{S}): T_{NI}^{S} is much different from $T_{NI}^{G}*$ due to the presence of a miscible nematic solvent inside the gel. The data of T_{NI} for the four systems will provide the basis to discuss this issue. Of further interest is that a mean-field theory[19–21] for nematic gel where the nematic ordering effect is considered on the basis of the Maier–Saupe concept predicts the volume transition as well as the reswelling behavior observed experimentally. The temperature dependence of the degree of equilibrium swelling in each system is quantitatively compared with the theoretical prediction.

II. MEAN FIELD THEORY FOR NEMATIC GEL IN NEMATIC SOLVENT

We describe here an outline of a mean field theory[19–21] for equilibrium swelling and phase behavior of a nematic gel in a nematic solvent. The mean field theory is originally for main-chain LC networks, but it may also be applicable to side-chain LC networks although the dangling mesogen–backbone polymer interaction and the effect of totally non-mesomorphic backbone on solubility are not explicitly introduced.[19–24] Chiu *et al.*[23,24] showed that the experimental phase diagrams for the mixtures of side-chain LC polymers and low molar mass nematic LC were well described by the mean field approach. They considered that the dangling mesogen–backbone polymer interaction had already been reflected in the nematic-isotropic transition temperature; the effect of nonmesomorphic backbone on solubility was reflected in the Flory–Huggins mixing interaction parameter.[23,24] As will be demonstrated later, along the same line, the mean field theory for nematic gel in nematic solvent also successfully describes the swelling and phase behavior of the side-chain LC networks in the LC solvents observed experimentally.

Consider a nematic gel composed of long flexible non-mesomorphic components (spacers) and rigid mesogens. The repeating unit on a network chain between adjacent cross-links consists of a mesogen occupying the number n_m of sites (segments) and a spacer occupying the number n_s of sites. The quantity n_m corresponds to the axial ratio of the mesogen. The total number of segments on a network chain n is given by $n = (n_m + n_s)t$ where t is the number of a repeating unit. The degree of equilibrium swelling Q is expressed as

$$Q = \frac{V}{V_0} = \frac{a^3 N_t}{a^3 n N_g} = \frac{1}{\phi}, \tag{1}$$

where $V = a^3 N_t$ and V_0 are the volumes of the network in the swollen and dry state, respectively, a^3 is the volume of an unit segment, and ϕ is the volume fraction of the network. The total number of unit cells N_t inside the gel is given by $N_t = n N_g + n_0 N_0$ where N_g and N_0 are the numbers of the network chains and solvents inside the gel, respectively, and n_0 is the axial ratio of the nematic solvent, i.e., the number of sites occupied by one nematic solvent molecule.

The total free energy of the nematic gel can be expressed as a sum of free energy of isotropic mixing F_{mix}, free energy of nematic ordering F_{nem}, free energy due to elasticity of nematic network F_{el}, as follows:

$$F = F_{\text{mix}} + F_{\text{nem}} + F_{el}. \tag{2}$$

The free energy of isotropic mixing F_{mix} may be described in terms of the Flory–Huggins theory:[25]

$$\frac{F_{mix}}{N_t kT} = \frac{(1-\phi)}{n_0} \ln(1-\phi) + \chi_{ms}\phi_m\phi_s + \chi_{m0}\phi_m(1-\phi) + \chi_{s0}\phi_s(1-\phi), \tag{3}$$

where k is the Boltzmann constant, T is the absolute temperature, $\phi_m = a^3 n_m t N_g / V = (1-p)\phi$ and $\phi_s = p\phi$ are the volume fractions of mesogen and spacer, respectively, and $p = n_s/(n_m + n_s)$ is the fraction of spacer segment. The quantities χ_{ms}, χ_{m0} and χ_{s0} are the Flory–Huggins isotropic mixing interaction parameters for mesogen–spacer segments, mesogen–solvent molecules, and spacer–solvent molecules, respectively. We assume hereafter $\chi = \chi_{ms} = \chi_{s0}$ and $\chi_{m0} = 0$. The latter means that the solvent acts as an athermal solvent for the mesogen.

The free energy of nematic ordering F_{nem} is given by the Maier–Saupe mean field theory[26,27] and its generalization to binary nematogens mixtures[23,24,28,29] as follows:

$$\frac{F_{\text{nem}}}{N_t kT} = \sum_{i=m,0} \frac{\phi_i}{n_i} f(\theta_i) \ln 4\pi f(\theta_i) d\Omega_i - \frac{1}{2} \nu_{mm} \phi_m^2 S_m^2 - \frac{1}{2} \nu_{00}(1-\phi)^2 S_0^2 - \nu_{m0}\phi_m(1-\phi)S_m S_0, \tag{4}$$

where Ω_i denotes the solid angle, θ_i ($i = m, 0$) is the angle between a reference axis and the director of each liquid crystal molecule. The subscripts m and 0 refer to the mesogen and the solvent inside the gel, respectively. The orientational order parameter of each nematogen S_i ($i = m, 0$) is defined as

$$S_i = \int \left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right) f(\theta_i) d\Omega_i. \tag{5}$$

The function $f(\theta_i)$ ($i = m, 0$) is the normalized orientation distribution function which may be expressed by

$$f(\theta_i) = \frac{1}{Z_i} \exp\left[\eta_i\left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right)\right], \tag{6}$$

where Z_i ($i = m, 0$) is the partition function defined as $Z_i = \int \exp[\eta_i(3\cos^2\theta_i - 1)/2]d\Omega_i$, and η_i ($i = m, 0$) is a dimensionless measure representing the strength of the nematic field. The quantity ν_{mm} is the Maier–Saupe nematic interaction parameter between the mesogens, ν_{00} is that between the solvent, and ν_{m0} is that between the mesogen and the solvent. The nematic-isotropic transition temperature of the pure solvent T_{NI}^{S} is related to ν_{00} via inverse dependence on T as[27]

$$\nu_{00} = \frac{4.54}{n_0}\left(\frac{T_{NI}^{S}}{T}\right). \tag{7}$$

In the simulations of T dependence of Q in Ref. 20 and 21, $\nu_{mm} = \nu_{m0} = \nu_{00}$ was assumed for simplicity even when me-

sogen of gel and nematic solvent were dissimilar. In the present study, it was needed to distinguish ν_{ij} ($i,j=m,0$) to obtain the satisfactory data-fit. The cross-interaction ν_{m0} is not known, thus we assume that ν_{m0} is proportional to $(\nu_{mm}\nu_{00})^{1/2}$ with a proportionality constant κ different from unity as[23,29]

$$\nu_{m0}=\kappa(\nu_{mm}\nu_{00})^{1/2}. \tag{8}$$

The constant κ characterizes the relative strength of the cross-interaction between the two dissimilar nematogens as compared to that in the same nematogens. The case $\kappa=1$ shows the intermediate coupling where the cross-interaction in the mixture has the same magnitude as that between the same nematogens in their pure states. The elastic free energy F_{el} for nematic network can be derived from the classical rubber elasticity theory combined with the freely jointed rod model as a function of ϕ and orientational order parameter of the mesogen S_m:[30,31]

$$\frac{F_{el}}{N_t kT}=\frac{3}{2n}\left\{\left[\frac{\phi}{n(1+2S_m)(1-S_m)^2}\right]^{1/3}+\frac{\phi}{3}\ln(1+2S_m)\right.$$
$$\left.\times(1-S_m)^2-\phi\left(1-\frac{2}{3}\ln\sqrt{n}\,\phi\right)\right\}. \tag{9}$$

When $S_m=0$, Eq. (9) accords with the elastic free energy of isotropic network. Warner et al.[19,22] derived another expression of F_{el} for nematic network. It is shown[31] that their expression has essentially the same form of Eq. (9) in the dilute systems ($\phi\ll1$); the use of their expression instead of Eq. (9) for F_{el} yields qualitatively the same results.

The relations between η_m, η_0, S_m and S_0 are evaluated by minimization of the free energy [Eq. (2)] with respect to S_m and S_0:

$$\eta_m=n_m[\nu_{mm}\phi_m S_m+\nu_{m0}(1-\phi)S_0]$$
$$-\frac{3n_m S_m}{n\phi_m(1+2S_m)(1-S_m)}$$
$$\times\left\{\left[\frac{\phi}{n(1+2S_m)(1-S_m)^2}\right]^{1/3}-\phi\right\} \tag{10}$$

and

$$\eta_0=n_0[\nu_{m0}\phi_m S_m+\nu_{00}(1-\phi)S_0]. \tag{11}$$

The order parameter of the pure solvent outside the gel (S_b) is given by Eqs. (5) and (6) ($i=b$) with

$$\eta_b=n_0\nu_{00}S_b. \tag{12}$$

Swelling equilibrium requires that the chemical potentials of the solvents inside and outside the gel (μ_0 and μ_0°, respectively) are equivalent:

$$\mu_0(\phi,S_m,S_0)=\mu_0^\circ(S_b). \tag{13}$$

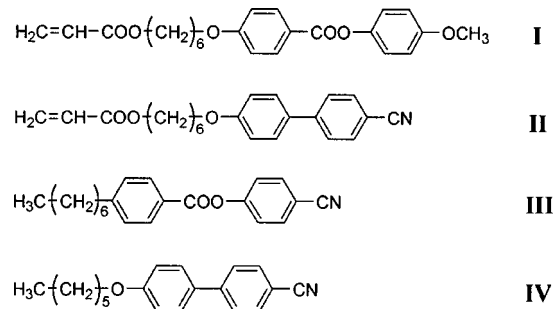Thus the equilibrium condition is obtained from Eq. (13) as follows:

FIG. 1. Molecular structures of the employed liquid crystalline monomers and solvents.

$$\frac{1}{n}\left\{\left[\frac{\phi}{n(1+2S_m)(1-S_m)^2}\right]^{1/3}-\phi\right\}+\frac{1}{n_0}\ln(1-\phi)+\frac{\phi}{n_0}$$
$$-\chi_{ms}p\,\phi^2(1-p)+\chi_{m0}(1-p\,\phi^2)+\chi_{s0}p\,\phi^2$$
$$+\frac{1}{2}\nu_{mm}S_m^2\phi_m^2+\nu_{m0}S_m S_0\phi_m(1-\phi)$$
$$+\frac{1}{2}\nu_{00}[S_0^2(1-\phi)^2-S_b^2]+\frac{1}{n_0}\ln\frac{Z_b}{Z_0}=0. \tag{14}$$

The equilibrium values of $Q(=1/\phi)$, S_m, S_0, and S_b as a function of T are determined by solving Eqs. (5) (for $i=m,0,b$) and (14) self-consistently.

III. EXPERIMENT

A. Sample preparation

Two side chain LC networks (designated as LCN-I and LCN-II) were prepared from the mesogenic acrylate monomers I and II (Fig. 1), respectively. The details of the preparation of these networks were described in our previous paper.[12] Molar ratio of monomer I or II, crosslinker (1,6-Hexanediol diacrylate) and initiator (2,2′-azobisiso butyronitrile) was 98:1:1. The cylindrical gels with the diameters of several hundreds micron were made by radical polymerization in capillaries. After the reaction, the gels were immersed in toluene to remove fully unreacted molecules. The gels were then gradually deswollen in mixtures of toluene and methanol by increasing the methanol content stepwise. The fully deswollen gels were completely dried in air. The dried gels were allowed to swell in a nematic LC solvent (molecule III or IV in Fig. 1). The nematic LC III with a quoted purity of at least 99% was purchased from Aldrich Co, and it was used as received without further purification. The nematic LC IV, synthesized by essentially the same method as in the case of the monomer II, was employed after purification. Nematic-isotropic transition temperatures T_{NI} of the dry LC networks and the LC solvents III and IV, which were estimated in cooling process by polarizing optical microscopy, are listed in Table I.

B. Swelling measurement and phase observation

Measurement of gel diameters and the phase observation were made as a function of temperature by a Nikon polarizing optical microscope E600 POL equipped with a Linkam

TABLE I. Nematic-isotropic transition temperatures of the liquid crystalline networks in the dry and swollen states and volume fractions of network in the vicinity of transition temperature.

| Network sample | $T_{NI}^{G*a}/°C$ | in LC III ($T_{NI}^S = 54.2$ °C) | | in LC IV ($T_{NI}^S = 74.9$ °C) | |
		$\phi_{NI}{}^b$	$T_{NI}^G/°C$	$\phi_{NI}{}^b$	$T_{NI}^G/°C$
LCN-I	125.4	0.0740	58.2 (59.5)^c	0.0534	77.7 (77.6)^c
LCN-II	131.2	0.183	71.0 (68.3)^c	0.131	79.6 (82.3)^c

^{a}In the dry state.
^{b}Volume fraction of network in the swollen phase at $T = T_{NI}^G + 0.2$ °C.
^{c}Calculated by Eq. (15).

LK-600PM sample stage under a nitrogen atmosphere. The details of the measurements were described elsewhere.[12] The surface level of LC solvent in an optical cell was adjusted to be low enough so that the LC phases inside the gels as well as the boundary of the gel surface were distinctly visible when viewed through the microscope (but high enough to immerse the gel completely). Degree of equilibrium swelling (Q) at each temperature was determined by the ratio of the gel diameters in the dry and swollen states (d_0 and d_s, respectively) using the definition of Q for isotropic swelling: $Q = V/V_0 = (d_s/d_0)^3$ where V and V_0 are the gel volumes in the swollen and dry states, respectively. The gels exhibited isotropic swelling even in the nematic phase because of the polydomain structure where the orientation of directors is globally random in space but a high orientational order is locally maintained.

IV. RESULTS

Part (a) of Figs. 2–5 shows the degree of equilibrium swelling (Q) as a function of temperature (T) for each of LCN-I and LCN-II swollen in the LC solvent III or IV (designated as LCN-I/III, LCN-I/IV, LCN-II/III, and LCN-II/IV, respectively). The data were obtained in cooling process. There exists the two independent nematic-isotropic transition temperatures T_{NI}^G and T_{NI}^S for the gel and the surrounding pure solvent, respectively. For all the systems examined here, T_{NI}^G is higher than T_{NI}^S. In the range $T < T_{NI}^G$, the nematic network and the miscible nematic solvent inside the gel form a single nematic phase. Phase separation inside the gel was not observed by polarizing microscopy with a typical magnification used in the studies[32,33] on phase separation of LC mixtures. As can be seen in Table I, the four systems show different T_{NI}^G depending on the network and the solvent used; T_{NI}^G of each swollen LC network is much depressed relative to T_{NI}^{G*} in the dry state due to the presence of a large amount of the miscible nematic solvent whose T_{NI}^S is fairly lower than T_{NI}^{G*}.

According to the LC phases inside and outside the gel, there exists three characteristic temperature regions: $T > T_{NI}^G$ where the whole system is isotropic; $T_{NI}^S < T < T_{NI}^G$ where the phase inside the gel is nematic, while the surrounding pure LC solvent is isotropic; $T < T_{NI}^S$ where the system is totally nematic. As is evident from part (a) of Figs. 2–5, the swelling behavior is closely related to the phase characteristics; all the systems examined show essentially the same correlation between the swelling and phase behavior. The descriptions

below are common to all the systems. In the totally isotropic phase ($T > T_{NI}^G$), Q is almost independent of T, although Q slightly decreases with decreasing in T for LCN-I/III and LCN-II/III. At T_{NI}^G, the isotropic gel discontinuously shrinks into the nematic gel: A discontinuous large decrease in gel volume, i.e., volume transition, takes place as a result of
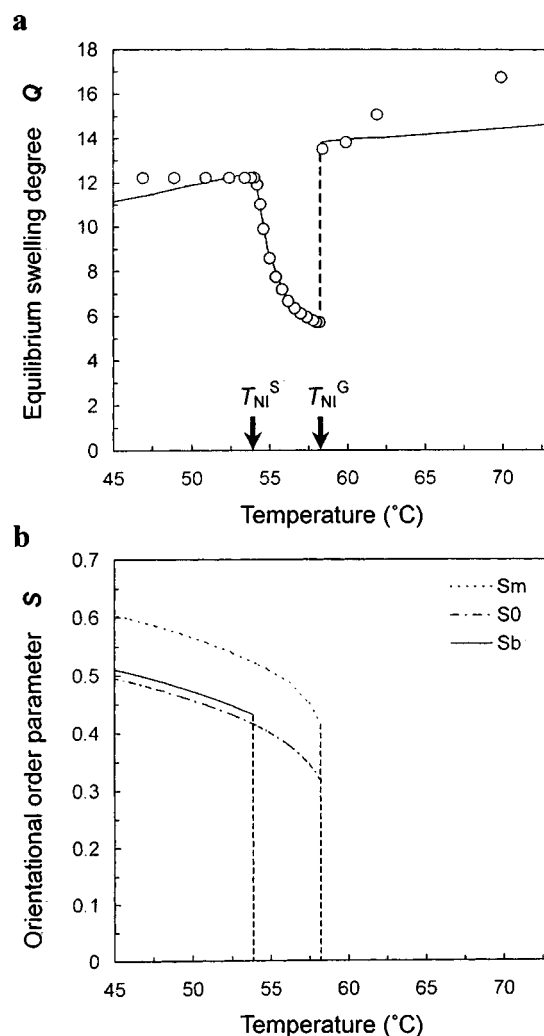
FIG. 2. (a) Equilibrium swelling degree (Q) of LCN-I in the LC solvent III as a function of T. The nematic-isotropic transition temperature of the gel (T_{NI}^G) and the surrounding pure LC solvent (T_{NI}^S) are 58.2 and 54.2 °C, respectively. The solid line represent the theoretical swelling curve calculated with $n = 120$, $n_m = 3.3$, $p = 0.23$, $n_0 = 2.5$, $\nu_{mm}/\nu_{00} = 1.05$, $\kappa = 0.966$, $\nu_{00}/\chi = 0.5$. (b) The orientational order parameters of the mesogen on network (S_m), the nematic solvents inside and outside gel (S_0 and S_b, respectively) as a function of T calculated using the same parameter values as (a).
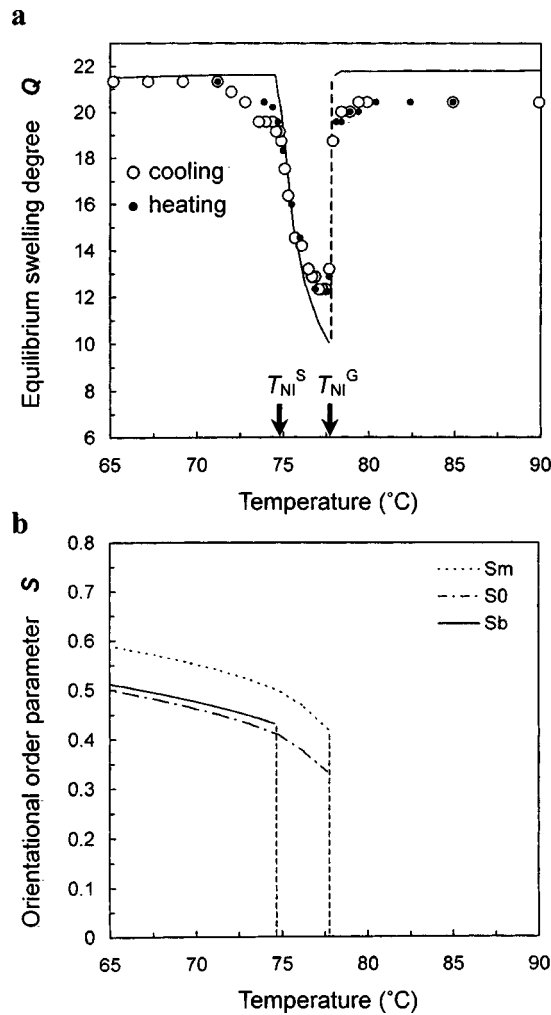
FIG. 3. (a) Equilibrium swelling degree (Q) of LCN-I in the LC solvent IV as a function of T. The nematic-isotropic transition temperature of the gel (T_{NI}^G) and the surrounding pure LC solvent (T_{NI}^S) are 77.7 and 74.9 °C, respectively. The solid line represent the theoretical swelling curve calculated with $n=120$, $n_m=3.3$, $p=0.23$, $n_0=2.55$, $\nu_{mm}/\nu_{00}=1.0$, $\kappa=0.985$, $\nu_{00}/\chi=1.0$. (b) The orientational order parameters of the mesogen on network (S_m), the nematic solvents inside and outside gel (S_0 and S_b, respectively) as a function of T calculated using the same parameter values as (a).

FIG. 4. (a) Equilibrium swelling degree (Q) of LCN-II in the LC solvent III as a function of T. The nematic-isotropic transition temperature of the gel (T_{NI}^G) and the surrounding pure LC solvent (T_{NI}^S) are 71.0 and 54.2 °C, respectively. The solid line represent the theoretical swelling curve calculated with $n=25$, $n_m=5.1$, $p=0.15$, $n_0=2.5$, $\nu_{mm}/\nu_{00}=1.0$, $\kappa=0.94$, $\nu_{00}/\chi=0.2$. (b) The orientational order parameters of the mesogen on network (S_m), the nematic solvents inside and outside gel (S_0 and S_b, respectively) as a function of T calculated using the same parameter values as (a).

nematic ordering inside the gel. The volume transition and the nematic-isotropic transition of the gel take place simultaneously and sharply within 0.2 °C. As temperature decreases further, Q of the shrunken nematic gel surrounded by isotropic LC solvent increases again. When temperature decreases down to $T \approx T_{NI}^S$, Q of the nematic gel reaches almost the same magnitude as Q in the totally isotropic phase ($T > T_{NI}^G$). It should be noted that the reentrant swelling occurs even in the case where the gap between T_{NI}^G and T_{NI}^S is rather narrow (for example, 2.8 °C for LCN-I/IV). At T_{NI}^S, nematic ordering of the surrounding solvent takes place, which does not cause discontinuous volume change but yields a kink of the Q-T curve. In the totally nematic phase ($T < T_{NI}^S$), Q is almost constant independently of T, and the magnitude is comparable to that in the totally isotropic phase ($T > T_{NI}^G$). Figure 6 displays the optical micrographs for LCN-I/IV in the three characteristic temperature regions which clearly show the correlations of Q with the phases
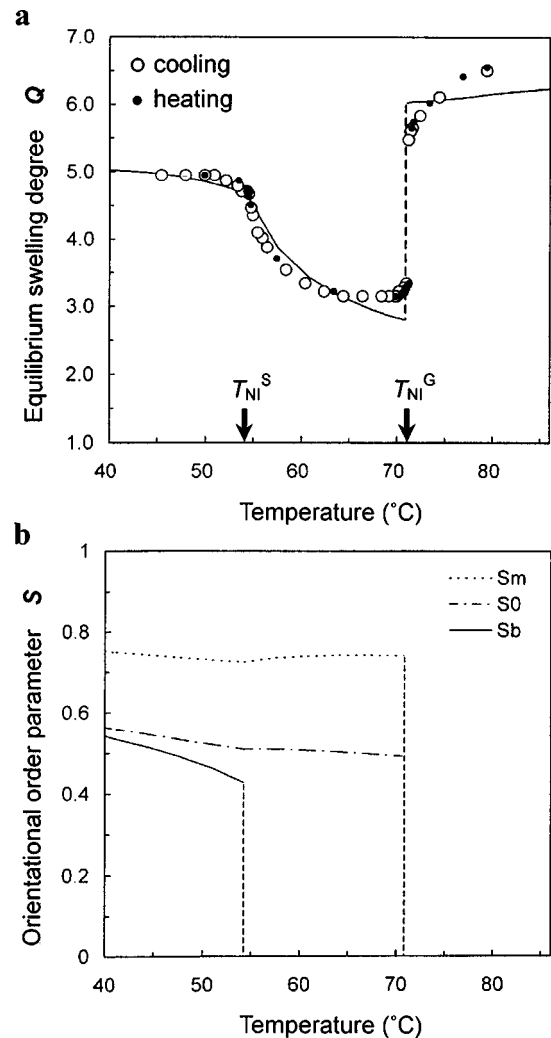
inside and outside the gel (also see Fig. 3 in Ref. 12 as the corresponding optical micrographs for LCN-I/III).

The T dependence of Q in heating process was also investigated for LCN-I/IV and LCN-II/III. As can be seen in Figs. 3 and 4, the significant effect of thermal history on the swelling and phase behavior was not observed except for a slight increase (within 0.5 °C) in T_{NI}^G on heating.

It should be emphasized that the nematic network in the similar nematogen (LCN-II/IV) exhibits essentially the same swelling behavior as other systems composed of the nematic networks and the dissimilar nematogens, although the magnitude of the discontinuous volume change in LCN-II/IV is fairly smaller. This indicates that the swelling characteristics such as volume transition and reswelling are not due to the dissimilarity between mesogen on network and nematogen.
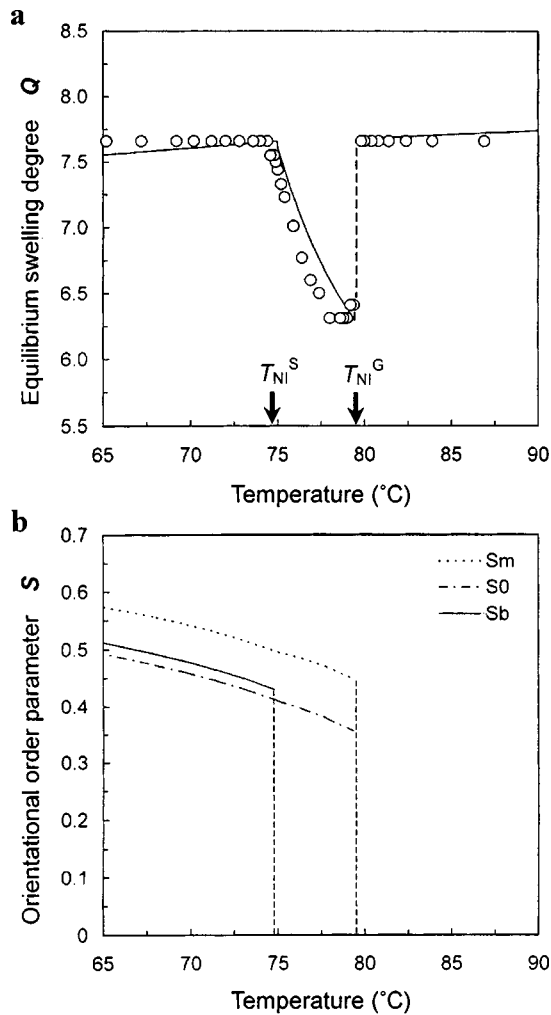
a

b

FIG. 5. (a) Equilibrium swelling degree (Q) of LCN-II in the LC solvent IV as a function of T. The nematic-isotropic transition temperature of the gel (T_{NI}^G) and the surrounding pure LC solvent (T_{NI}^S) are 79.6 and 74.9 °C, respectively. The solid line represent the theoretical swelling curve calculated with $n=25$, $n_m=3.52$, $p=0.15$, $n_0=2.55$, $\nu_{mm}/\nu_{00}=1.0$, $\kappa=0.948$, $\nu_{00}/\chi=0.34$. (b) The orientational order parameters of the mesogen on network (S_m), the nematic solvents inside and outside gel (S_0 and S_b, respectively) as a function of T calculated using the same parameter values as (a).

V. DISCUSSION

A. Phase transition temperatures

It is seen in Table I that T_{NI}^G for the swollen LC gels is much reduced relative to $T_{NI}^{G}*$ for the corresponding pure LC networks. This is qualitatively because the gel contains a large amount of the miscible nematic solvent whose T_{NI}^S is rather lower than $T_{NI}^{G}*$. We have found that the relation among T_{NI}^G, $T_{NI}^{G}*$, and T_{NI}^S is well expressed by the following simple additivity:

$$T_{NI}^G = (1-\phi_{NI})T_{NI}^S + \phi_{NI}T_{NI}^{G}*,\qquad(15)$$

where ϕ_{NI} is the volume fraction of network in the vicinity of T_{NI}^G ($T=T_{NI}^G+0.2\,°C$) in the swollen phase. This equation is entirely phonomenological, but as can be seen in Table I, T_{NI}^G calculated by Eq. (15) are fairly close to the data for all the systems. This good agreement is surprising, because T_{NI}^G where the order parameter inside the gel jumps from zero to
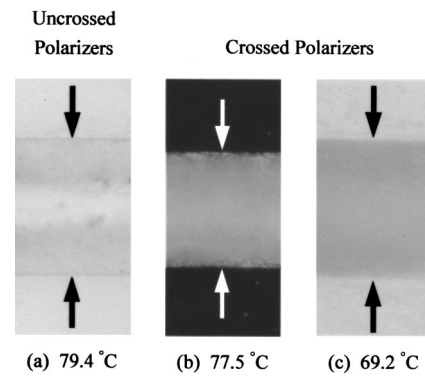
a finite value is a complicated function of many variables as is evident from Eqs. (5), (10), and (11). The values of ϕ_{NI} for the gels examined here are relatively small (i.e., relatively dilute system), which may apparently simplify the relation between T_{NI}^G, $T_{NI}^{G}*$, and T_{NI}^S. Investigation of T_{NI}^G for a LC gel with higher cross-linking density exhibiting higher ϕ_{NI} (i.e., less swellability) will be helpful to understand this issue, which will be performed in our future study.

In the present study, T_{NI}^G is higher than T_{NI}^S for all the systems examined. If a nematogen whose T_{NI}^S is higher than $T_{NI}^{G}*$ is employed as swelling solvent, T_{NI}^G may be lower than T_{NI}^S: In the case of LCN-I and LCN-II, a nematic solvent with T_{NI}^S over at least 130 °C is required. The thermal instability of the LC networks and the LC solvents precluded the equilibrium swelling measurement at high temperatures over 130 °C. It is needed to prepare a LC gel with a fairly lower $T_{NI}^{G}*$, which will be carried out in our separate study. Meanwhile, it is very difficult to make T_{NI}^G coincide with T_{NI}^S experimentally. Even if a mesogen on network and a nematic solvent are similar as in the case of LCN-II/IV, there exists a finite difference between T_{NI}^G and T_{NI}^S: The mesogen is attached to network backbone, which yields a difference in thermal stability of nematic phase between the gel and the equivalent pure nematogen.

B. Comparison of experimental swelling temperature curves with theoretical prediction

In this section, the experimental data are compared with the predictions of the mean field theory for nematic gel. The lines in parts (a) and (b) of Figs. 2–5 represent the theoretical curves for Q and S_i ($i=m,0,b$), respectively. The quantities n_0, n, n_m, p, ν_{00}/χ, ν_{mm}/ν_{00}, κ were used as fitting parameters. As can be seen in the figures, the swelling and phase characteristics observed are well described by the theory, and the calculated swelling curves satisfactorily agree with the experimental data of all the systems. The theory contains many fitting parameters, but these fitting parameters

Uncrossed Polarizers   Crossed Polarizers

(a) 79.4 °C   (b) 77.5 °C   (c) 69.2 °C

FIG. 6. Optical micrographs for the cylindrical LC gel LCN-I swollen in the nematic solvent IV. Arrows indicate the boundary of the gel surface. The pictures represent (a) totally isotropic phase at $T>T_{NI}^G$; (b) nematic phase inside the gel and isotropic phase outside the gel at $T\approx T_{NI}^G$; (c) totally nematic phase at $T<T_{NI}^S$. The micrographs also show that ca. 40% reduction in gel volume (ca. 15% reduction in gel diameter) takes place as a result of the nematic-isotropic phase transition inside the gel; the gel diameter in the totally nematic phase (c) is comparable to that in the totally isotropic phase (a).

only alter the magnitudes of Q and T_{NI}^G. The successful data fit is substantially attributed to the framework of the mean field theory. The mean field approach assuming monodomain LC structure in nematic phase may not be directly applicable to polydomain systems, but the good predictive capability demonstrated here suggests that the errors are fairly small for equilibrium swelling degree. The parameter values characterizing each nematic network or solvent were fixed in the data fitting for different systems: $n_0 = 2.5$ for the solvent III, $n_0 = 2.55$ for the solvent IV, $n = 120$, $n_m = 3.3$, and $p = 0.23$ for LCN-I, $n = 25$, $p = 0.15$ for LCN-II were consistently employed. The different values for n_m of LCN-II, however, were required to achieve the good data fit in LCN-II/III and LCN-II/IV. Although the mesogen of LCN-II and the nematogen IV are similar, the fitted values of n_m and n_0 are not identical. As mentioned before, the dangling mesogen–network backbone interaction significantly influences the thermal stability of the nematic phase of the mesogen. For example, $T_{NI}^{G}*$ for the dry LCN-II is much higher than T_{NI}^S of the LC IV. The similar tendency is known for uncross-linked side-chain type LC polymers.[34,35] The side group mesogen–network backbone interaction is reflected in n_m or ν_{mm} in the theory. The amounts of crosslinker truly introduced during synthesis are presumably lower than that given by the crosslinker concentration (1 mol %) in preparation, because the crosslinking efficiency is reduced by the presence of the mesogen. However, it should be noted that each LC network exhibited good reproducibility for Q: The difference in Q between the samples made separately was within 10%. This is why the same value of n was employed for each LC network in different solvents.

The T dependence of each order parameter not only agrees with the phase observation, but also indicates that the swelling behavior is mainly governed by orientational order of each LC molecule. The equilibrium swelling in the totally isotropic phase ($T > T_{NI}^G$ where there exists no orientational order) corresponds to the familiar case, namely, swelling of isotropic network in isotropic solvent. In this region, the T dependence of Q is mainly controlled by isotropic mixing interaction. The weak T dependence of Q in the totally isotropic phase stems from the weak T dependence of $\chi (\sim 1/T)$. At T_{NI}^G, the order parameters S_m for mesogen on network and S_0 for the solvent inside the gel simultaneously jump from zero to finite values, which accords with the observation that the nematic network and the nematic solvent inside the gel form a single nematic phase. The theory demonstrates that the jump of S_m and S_0, i.e., nematic ordering inside the gel, causes a discontinuous volume decrease (volume transition). In the region $T_{NI}^S < T < T_{NI}^G$, the nematic order inside the gel (S_m and S_0) increases with decreasing in T in a similar way as S of general LC in the nematic phase does,[27,36] whereas the surrounding solvent remains isotropic ($S_b = 0$). This indicates that the reswelling, i.e., an uptake of the surrounding isotropic LC solvent by the nematic network, is thermodynamically induced by an increase in orientational order inside the gel. The theoretical swelling curve has an inflection at T_{NI}^S as a result of the jump of S_b from zero to a finite value. Nematic ordering of the pure solvent outside the gel does not cause an instability in the chemical

potential of the gel, and consequently, the gel volume changes continuously at T_{NI}^S. The order parameters inside the gel still increase with decreasing in T in the totally nematic phase ($T < T_{NI}^S$), which does not yield further swelling in contrast to the region $T_{NI}^S < T < T_{NI}^G$. When the nematic orders inside and outside the gel are comparable, the growth of the nematic order inside the gel does not significantly alter the degree of equilibrium swelling. It should be emphasized again that a further swelling induced by an increase in nematic order inside the gel occurs when there exists no nematic order in the surrounding solvent ($S_b = 0$).

In the mean field theory, the difference between T_{NI}^G and T_{NI}^S mainly depends on n_m/n_0, ν_{mm}/ν_{00} and κ. As each of these values increases, the ratio T_{NI}^G/T_{NI}^S becomes higher. High axial ratio of mesogen (n_m) as well as large nematic interaction between mesogens on network (ν_{mm}) stabilizes the nematic phase of the gel, which increases T_{NI}^G. An increase in κ representing cross-interaction between mesogen on network and nematic solvent also stabilizes the nematic phase of the gel comprising the mixture of the mesogen and the solvent. For all the systems, the fitted values of κ are less than unity. This agrees with the results ($\kappa < 1$) reported for general LC mixtures:[23,28,29] Unless there exists strong cross-interaction between the two dissimilar nematogens, κ is less than unity.

In the case of nonionic isotropic gels such as N-isopropylacrylamide gel, a specific dependence of χ (polymer-solvent mixing interaction) on temperature and/or polymer concentration is an important key to the volume transition phenomena.[11] Meanwhile, in the case of nematic gel, none of the isotropic mixing interactions between mesogen, spacer and solvent does not play an important role in the volume transition and reentrant swelling, although they influence the magnitude of Q. The characteristic swelling behavior is observed even in the system with $\chi_{m0} \approx 0$ (LCN-II/IV; a nematic network in a similar nematogen); even if $\chi (= \chi_{ms} = \chi_{s0}) = 0$ is assumed, the theory predicts that nematic gel exhibits the volume transition as well as reentrant swelling. Thus nematic order is a governing force for the characteristic swelling behavior of nematic gel.

As mentioned before, the mean-field theory is originally derived on the basis of main-chain LC network. The dangling mesogen–network backbone interaction in side-chain LC polymers is not explicitly introduced in the mean field theory. This interaction appears mainly in T_{NI}^G, and as a result, it is reflected in n_m and ν_{mm} in the data fit as in the case of the mixtures of side-chain LC polymers and nematic solvents.[23,24] The backbone of side-chain LC network is totally composed of nonmesomorphic components, which may influence on the solubility. This is important in isotropic solvent system, but minor in nematic solvent: As described before, even if we drop the isotropic mixing interaction parameters (χ) in the free energy, the theory predicts essentially the swelling features, i.e., volume transition and reswelling behavior. The use of the conventional χ parameter is sufficient to reflect the effect of totally nonmesomorphic backbone on solubility. Thus, as in the case of the mixtures of side-chain LC polymers and nematic solvent,[23,24] the mean field theory is at least qualitatively successful in describing the swelling

and phase behavior of the side-chain LC gels in nematic solvent. The comparison of the swelling and phase behavior between main- and side-chain LC gels comprising identical mesogens will provide us important information about this issue. This is a subject in our future study.

VI. CONCLUSIONS

The equilibrium swelling behavior of nematic network in miscible nematic solvent is mainly governed by nematic (orientational) orders of the LC molecules inside and outside the gel. The degree of equilibrium swelling (Q) is almost independent of T in the totally isotropic phase ($T > T_{NI}^G$) where there exists no orientational order in the system as well as in the totally nematic phase ($T < T_{NI}^S$) where the nematic orders inside and outside the gel are comparable. Meanwhile, Q is strongly T dependent in the region $T_{NI}^S < T < T_{NI}^G$ where there exists a finite nematic order inside the gel whereas nematic order outside the gel is absent. When the isotropic swollen gel is cooled down to T_{NI}^G, the nematic ordering inside the gel takes place, which simultaneously causes a discontinuous reduction in gel volume (nematic ordering-induced volume transition); that is, the isotropic swollen gel is discontinuously collapsed into the nematic gel. When the system is further cooled, the shrunken nematic gel swells again with descending in T as a result of an increase in nematic order inside the gel. Due to this reswelling, Q of the nematic gel at $T \approx T_{NI}^S$ becomes comparable to that in the totally isotropic phase. At T_{NI}^S, the nematic ordering of the solvent outside the gel occurs, which yields a kink of the Q-T curves without discontinuity. No significant effect of thermal hysteresis on the swelling and phase behavior is observed. The correlation between swelling and phase characteristics does not depend on the details of chemical structures of mesogen on network and nematic solvent. A nematic network in a similar nematogen also undergoes a nematic ordering induced-volume transition as well as a reswelling in the range in $T_{NI}^S < T < T_{NI}^G$. The experimental Q-T curves and the phase behavior observed are successfully described by a mean field theory where nematic ordering effect is considered on the basis of the Maier–Saupe concept. The theory also demonstrates that nematic order of LC molecule is a governing force for swelling of nematic gel: The nematic-isotropic transition inside gel drives a volume transition; an increase in nematic order inside gel thermodynamically induces a further swelling of nematic gel surrounded by isotropic LC solvent.

[1] K. Dusek and D. Patterson, J. Polym. Sci., Part A-2 **6**, 1209 (1968).
[2] T. Tanaka, Phys. Rev. Lett. **40**, 820 (1978).
[3] T. Amiya and T. Tanaka, J. Chem. Phys. **86**, 2375 (1987).
[4] M. Annaka and T. Tanaka, Nature (London) **355**, 430 (1992).
[5] S. Kang and Y. H. Bae, Macromolecules **34**, 8173 (2001).
[6] Y. Hirokawa, T. Tanaka, and E. S. Matsuo, J. Chem. Phys. **81**, 6379 (1984).
[7] F. Ilmain, T. Tanaka, and E. Kokufuta, Nature (London) **349**, 400 (1991).
[8] M. Tokita and T. Tanaka, Science **253**, 1121 (1991).
[9] S. Seelenmeyer, I. Deike, S. Rosenfeldt, C. Norhausen, N. Dingenouts, M. Ballauff, T. Narayanan, and P. Lindner, J. Chem. Phys. **114**, 10471 (2001).
[10] X. Z. Zhang, Langmuir **17**, 6094 (2001).
[11] M. Shibayama and T. Tanaka, Adv. Polym. Sci. **109**, 1 (1993).
[12] K. Urayama, Y. Okuno, T. Kawamura, and S. Kohjiya, Macromolecules **35**, 4567 (2002).
[13] T. Okano, Adv. Polym. Sci. **110**, 180 (1993).
[14] R. Yoshida, K. Uchida, Y. Kaneko, K. Sakai, A. Kikuchi, Y. Sakurai, and T. Okano, Nature (London) **374**, 240 (1995).
[15] C. Alvarez-Lorenzo and A. Concheiro, J. Controlled Release **80**, 247 (2002).
[16] R. Zentel, Liq. Cryst. **1**, 589 (1986).
[17] R. Kishi, Y. Suzuki, H. Ichijo, and O. Hirasa, Chem. Lett. **1994**, 2257.
[18] R. Kishi, Y. Suzuki, H. Ichijo, and O. Hirasa, Mol. Cryst. Liq. Cryst. **295**, 113 (1997).
[19] X. J. Wang and M. Warner, Macromol. Theory Simul. **6**, 37 (1997).
[20] A. Matsuyama and T. Kato, Phys. Rev. E **64**, 010701 (2001).
[21] A. Matsuyama and T. Kato, J. Chem. Phys. **116**, 8175 (2002).
[22] M. Warner, K. P. Gelling, and T. A. Vilgis, J. Chem. Phys. **88**, 4008 (1988).
[23] H.-W. Chiu and T. Kyu, J. Chem. Phys. **103**, 7471 (1995).
[24] H.-W. Chiu, Z. L. Zhou, T. Kyu, G. L. Cada, and L. C. Chien, Macromolecules **29**, 1051 (1996).
[25] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
[26] W. Maier and A. Z. Saupe, Naturforsh, A. **14a**, 882 (1959).
[27] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals*, 2nd ed. (Oxford University Press, New York, 1993).
[28] F. Brochard, J. Jouffroy, and P. Levinson, J. Phys. (France) **45**, 1125 (1984).
[29] F. Benmouna, U. Maschke, X. Coqueret, and M. Benmouna, Polym. Int. **50**, 469 (2001).
[30] F. Brochard, J. Phys. (France) **40**, 1049 (1979).
[31] A. Matsuyama and T. Kato, J. Chem. Phys. **114**, 3817 (2001).
[32] F. Benmouna, J. Ruhe, and D. Johannsmann, Liq. Cryst. **26**, 1655 (1999).
[33] D. Nwabunma and T. Kyu, Macromolecules **32**, 664 (1999).
[34] N. A. Plate and V. P. Shivaev, *Comb-shaped Polymers and Liquid Crystals* (Plenum, New York, 1987).
[35] D. J. Simmonds, in *Liquid Crystalline Polymers: From Structures to Applications*, edited by A. A. Collyer (Elsevier Applied Science, London, 1992).
[36] S. Chandrasekhar, *Liquid Crystals*, 2nd ed. (Cambridge University Press, Cambridge, 1992).