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Volume Phase Transition of Liquid Crystalline Gels in a Nematic Solvent

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Some swollen polymer networks (gels) are known to undergo a discontinuous large volume change of gels in response to an infinitesimal change of an environmental intensive variable such as solvent composition,[1−3] pH,[4,5] temperature,[6−11] electric field,[12] and light.[13] These volume phase transitions of gels are driven by the competition between repulsive and attractive molecular interactions on the polymer networks which are classified into four categories: van der Waals, hydrophobic, ionic, hydrogen bonding.[7,14] Some theoretical studies[15−19] have suggested that orientational (nematic) ordering effect can also induce a volume transition of gel. A mean-field theory shows that a gel with nematic liquid crystallinity immersed in isotropic solvents[15−17] or nematogens[15,18,19] exhibits a volume transition triggered by orientational ordering inside the gel and that the degree of swelling as a function of temperature is mainly controlled by orientational order of liquid crystalline (LC) molecules. In contrast to these theoretical developments, no experimental study has been accomplished to clarify the correlation between the swelling and phase behavior of nematic gels. There exists some experimental studies[20,21] for some nematic gels swollen in nematic solvents, but their main focuses were on deformation of the gels under electric field; they did not elucidate the relation between the degree of swelling and the phase of the liquid crystals. In the case of an isotropic (polybutadiene) gel swollen in some nematic solvents, the nematic−isotropic transition of the solvents was found to yield no significant change in gel volume.[22,23]

In the present study, swelling behavior has been experimentally studied for two different nematic LC gels in a nematic solvent whose nematic−isotropic phase transition temperature (T_{NI}^{S}) is lower than those of the gels (T_{NI}^{G}). In particular, the degree of equilibrium swelling of the nematic gel in the vicinity of the two nematic−isotropic transition temperatures has been critically investigated. We have first demonstrated that the LC gel discontinuously shrinks into the nematic state at T_{NI}^{G} and that, at further decreased temperatures, the shrunken nematic gel exhibits a continuous reswelling (reentrant swelling) in the region $T_{NI}^{S} < T < T_{NI}^{G}$. These characteristics of swelling and phase behavior observed qualitatively accord with the predictions of a mean-field theory for nematic gel.

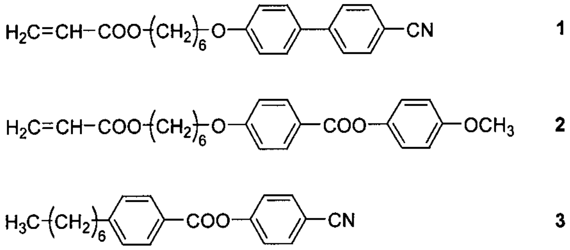

Figure 1. Molecular structures of the employed liquid crystalline monomers and solvent.

Two different nematic LC gels, each of which is composed of nematic LC monomer **1** or **2** (Figure 1), were prepared by free radical polymerization. The mesogenic acrylate monomers **1** and **2** were prepared by the methods reported by Sibaev et al.[24] and Ringsdorf et al.,[25] respectively. 1,6-Hexanediol diacrylate and 2,2′-azobis(isobutyronitrile) were employed as cross-linker and initiator, respectively. The molar ratio of each monomer, cross-linker, and initiator was 98:1:1. The reactant mixture was dissolved in toluene so that the concentration of monomer **1** and **2** would be 4.65×10^{-3} and 3.24×10^{-3} mmol/μL, respectively. The solution was polymerized in capillaries of inner diameter of 0.41 mm at 80 °C. The gels were extracted from the capillaries, washed with toluene, and deswelled gradually using mixtures of toluene and methanol with a series of compositions. After deswelling in pure methanol, the gels were dried and allowed to swell in a nematic LC solvent (molecule **3** in Figure 1). The LC solvent with a quoted purity of at least 99% was used without further purification. Cross-polarizing microscopy revealed that the LC solvent **3** was completely miscible with each of the LC monomers **1** and **2** regardless of mixing ratio.

Measurement of gel diameters and the phase observation were made as a function of temperature by a Nikon polarizing optical microscope equipped with a Linkam LK-600PM under a nitrogen atmosphere. The temperature was controlled with an accuracy of better than ±0.03 °C. The surface level of the LC solvent was adjusted to be low enough so that the phases of the LC inside the gels and the boundary of the gel surface were distinctly visible when viewed through the microscope (but high enough to immerse the gel completely). The equilibrium swollen gels at various temperatures as viewed in the polarizing microscope were photographed, and the diameter of the cylindrical gels at each temperature was measured on the enlarged photograph. The degree of equilibrium swelling (Q) was determined by the ratio of the gel diameters in the dry and swollen states (d_0 and d_s, respectively) as $Q = V/V_0 = (d_s/d_0)^3$, where V and V_0 are the gel volumes in the swollen and dry states, respectively. This definition of Q is valid for isotropic swelling, and it is to be noted that the gels swelled isotropically even in the nematic phase because under no aid of external field such as electric field the nematogens form a polydomain structure where the direction of principal axis of orientation (director) is globally random in space but a high orientational order is locally maintained.

Figure 2 illustrates the swelling curves obtained as temperature was decreased. Both the two systems have essentially the same characteristics for the swelling and phase behavior. The descriptions given below are common to both the systems. Two characteristic tempera-

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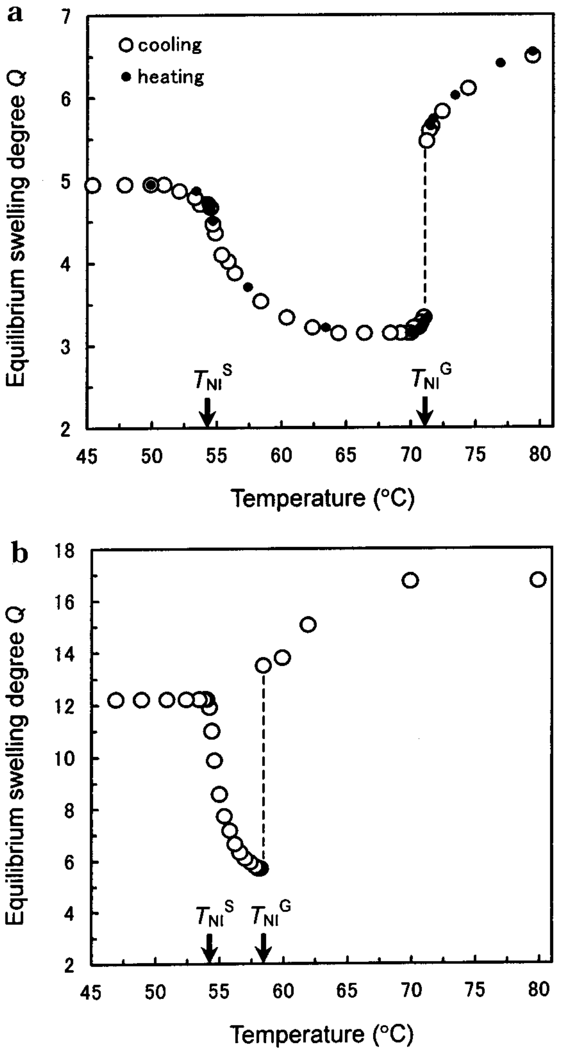

Figure 2. Equilibrium swelling degree (Q) of two different liquid crystalline gels, each of which is composed of monomer (a) **1** or (b) **2** in nematic liquid crystalline solvent **3** as a function of temperature. The nematic–isotropic phase transition temperatures T_{NI}^G and T_{NI}^S are those for the gel and the solvent outside the gel, respectively. The solvent inside the gel forms a single nematic phase with the liquid crystalline gels at temperatures below T_{NI}^G.

tures for the nematic–isotropic phase transition (T_{NI}^G and T_{NI}^S) were observed: One is for the pure LC solvent outside the gel (T_{NI}^S), and the other is for the gel (T_{NI}^G). In both the two systems investigated here, T_{NI}^G was higher than T_{NI}^S. At temperatures above T_{NI}^G where the whole system is in an isotropic phase, Q slightly decreases with decreasing in temperature. At $T = T_{NI}^G$ ($T_{NI}^G = 71.0$ and 58.2 °C upon cooling for the LC gels made of monomer **1** and **2**, respectively), the gel and the LC solvent *inside* the gel become a nematic phase, and the gel shows a discontinuous large decrease in volume. Note that T_{NI}^G is not the nematic-to-isotropic phase transition temperature of a pure (solvent-free) LC network but that of a LC network containing LC solvent. The temperatures T_{NI}^G are fairly lower than the phase transition temperatures of the corresponding pure LC networks due to the presence of the miscible LC solvent with a lower phase transition temperature, the details of which will be discussed in a separate publication. Parts a and b of Figure 3 show the optical micrographs for the cylindrical LC gel made of monomer **2** in the LC solvent **3** at 58.4 °C (= T_{NI}^G + 0.2 °C) and 58.2 °C (= T_{NI}^G), respectively. The discontinuity of the T dependence of Q at T_{NI}^G is evident, since the large volume change occurs within the small temperature difference of 0.2 °C. The gel and the LC solvent inside the gel form a single nematic phase at temperatures of $T \leq T_{NI}^G$, and no phase separation inside the gel was confirmed using thin films of the LC gels by polarizing microscopy with a typical magnification employed in the studies of phase separation of LC mixtures.[26,27]

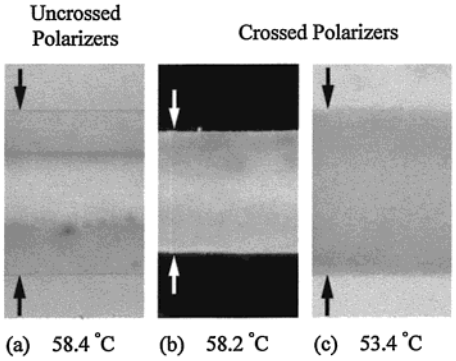

Figure 3. Optical micrographs for the cylindrical liquid crystalline gel made of monomer **2** swollen in the nematic solvent **3**. The pictures represent (a) isotropic phase inside and outside the gel at 58.4 °C (= T_{NI}^G + 0.2 °C), (b) nematic phase inside the gel and isotropic phase outside the gel at 58.2 °C (= T_{NI}^G), and (c) nematic phase inside and outside the gel at 53.4 °C (<T_{NI}^S). Arrows indicate the boundary of the gel surface. The micrographs also show that ca. 30% reduction in gel diameter (ca. 100% reduction in gel volume) takes place discontinuously as a result of the nematic–isotropic phase transition of the gel at T_{NI}^G and that the diameter of the equilibrium swollen gel in the totally nematic phase (c) is comparable to that in the totally isotropic phase (a).

In the temperature region $T_{NI}^S < T \leq T_{NI}^G$ where each of the phases inside and outside the gel is nematic or isotropic, respectively, the gel shows a continuous reswelling with decreasing in temperature. In addition to volume phase transition, this reentry swelling phenomenon is also characteristic of the LC gels in the LC solvent. As temperatures decrease further, the LC solvent outside the gel becomes a nematic phase at T_{NI}^S = 54.2 °C. At T_{NI}^S, the swelling curve shows an inflection. In the temperature region $T \leq T_{NI}^S$ where both the phases outside and inside the gel are nematic, Q is almost independent of T, and the magnitude of Q is comparable to those in the isotropic phase. Figure 3c shows the optical micrograph for the gel at 53.4 °C (< T_{NI}^S). The swelling data obtained in heating process are also displayed in Figure 2a. No significant thermal hysteresis of swelling and phase behavior was observed except for a slight increase (0.5 °C) in T_{NI}^G (and volume transition temperature) upon heating.

The swelling characteristics of the LC gels are closely related to phases of LC molecules inside and outside the gels, which suggests that orientational orders of LC molecules are responsible for the volume transition and the reentry swelling behavior. The degree of orientational order of LC molecules is represented by so-called orientational order parameter S.[28,29] As temperature decreases, at T_{NI}^G, each of the orientational order parameters of the mesogens of the gel and the LC solvent inside the gel (denoted as S_m and S_0, respectively) discontinuously jumps from zero to a finite value as a result of the nematic–isotropic phase transition. This nematic ordering inside the gel drives the collapse of the gel. In the temperature region $T_{NI}^S < T < T_{NI}^G$, nematic order inside the gel (S_m and S_0) increases further with decreasing T in a similar way as S of general LC in nematic phase does.[28,29] The resulting increase in nematic interaction inside the gel is expected to induce thermodynamically the uptake of LC solvent outside the gel by the network, i.e., reswelling. It is very important to mention that a mean-field theory[19] for nematic gel in nematic solvent, in which nematic ordering effects are considered on the basis of the Maier−Saupe interactions, successfully reproduces the major characteristics of the swelling and phase behavior obtained here: volume phase transition at T_{NI}^G; formation of single nematic phase of the gel and the LC solvent inside the gel at T_{NI}^G; reswelling in the temperature region $T_{NI}^S < T < T_{NI}^G$; inflection of T dependence of Q at T_{NI}^S; weak T dependence of Q at temperatures of $T > T_{NI}^G$ and $T < T_{NI}^S$ (see Figures 3 and 4 in ref 19). It is theoretically shown that a jump of S_m and S_0 yields a discontinuous volume change of gel[18,19] and that reswelling is thermodynamically induced when S_m and S_0 increase in the surrounding of isotropic LC solvent ($S_b = 0$).[19] A jump of the order parameter of the bulk LC solvent outside the gel S_b does not cause instability in chemical potential of the LC gel, which explains the continuous volume change at T_{NI}^S. As mentioned before, the swelling is isotropic even in nematic phase due to polydomain LC structure. The mean-field theory assuming monodomain structure may not be directly applicable to the experimental results, but the qualitative good agreement suggests that the errors are rather small. Quantitative fitting of the mean-field theoretical prediction to the experimental data will be made in a separate publication. It is to be emphasized that interactions related to solubility between different molecules have no significant contribution to volume phase transition of LC gel. Actually, the aforementioned mean-field theoretical predictions for the swelling of nematic gel in nematic solvent are derived under the assumptions that a LC solvent acts as good solvent for the mesogen on LC gel regardless of phase of LC and that the nonmesomorphic component (spacer)−nematogen interaction parameter (χ) simply depends on T as $\chi \sim 1/T$ over the whole temperatures.[19] Note that a specific dependence of χ on T and/or Q must be assumed in order to describe theoretically the known volume phase transitions of nonionic isotropic gels such as *N*-isopropylacylamide gel.[14] Thus, nematic ordering must be a driving force for the volume transition and the reentry swelling of the LC gels.

Further experimental surveys for the swelling behavior of a system with $T_{NI}^S > T_{NI}^G$ as well as volume transition of LC gel in nonnematogenic solvent are now in progress, and they will reveal further the details of nematic ordering effect on swelling and phase behavior of LC gel.

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References and Notes

(1) Dusek, K.; Patterson, D. *J. Polym. Sci., Part A-2* **1968**, *6*, 1209.
(2) Tanaka, T. *Phys. Rev. Lett.* **1978**, *40*, 820.
(3) Amiya, T.; Tanaka, T. *J. Chem. Phys.* **1987**, *86*, 2375.
(4) Annaka, M.; Tanaka, T. *Nature (London)* **1992**, *355*, 430.
(5) Kang, S.; Bae, Y. H. *Macromolecules* **2001**, *34*, 8173.
(6) Hirokawa, Y.; Tanaka, T.; Matsuo, E. S. *J. Chem. Phys.* **1984**, *85*, 6379.
(7) Ilmain, F.; Tanaka, T.; Kokufuta, E. *Nature (London)* **1991**, *349*, 400.
(8) Tokita, M.; Tanaka, T. *Science* **1991**, *253*, 1121.
(9) Grinberg, V. Y.; Grinberg, N. V.; Mikheeva, L. M.; Dembo, A. T.; Makhaeva, E. E.; Khokhlov, A. R.; Grosberg, A. Y.; Tanaka, T. *Macromol. Chem. Phys.* **1999**, *200*, 1603.
(10) Seelenmeyer, S.; Deike, I.; Rosenfeldt, S.; Norhausen, C.; Dingenouts, N.; Ballauff, M.; Narayanan, T.; Lindner, P. *J. Chem. Phys.* **2001**, *114*, 10471.
(11) Zhang, X. Z. *Langumuir* **2001**, *17*, 6094.
(12) Tanaka, T.; Nishio, I.; Sun, S.-T.; Ueno-Nishio, S. *Science* **1982**, *218*, 467.
(13) Suzuki, A.; Tanaka, T. *Nature (London)* **1990**, *346*, 345.
(14) Shibayama, M.; Tanaka, T. *Adv. Polym. Sci.* **1993**, *109*, 1.
(15) Brochard, F. *J. Phys. (Paris)* **1979**, *40*, 1049.
(16) Warner, M.; Wang, X. J. *Macromolecules* **1992**, *25*, 445.
(17) Matsuyama, A.; Kato, T. *J. Chem. Phys.* **2001**, *114*, 3817.
(18) Wang, X. J.; Warner, M. *Macromol. Theory Simul.* **1997**, *6*, 37.
(19) Matsuyama, A.; Kato, T. *Phys. Rev. E* **2001**, *64*, 010701.
(20) Zentel, R. *Liq. Cryst.* **1986**, *1*, 589.
(21) Kishi, R.; Suzuki, Y.; Ichijo, H.; Hirasa, O. *Chem. Lett.* **1994**, 2257.
(22) Urayama, K.; Luo, Z.; Kawamura, T.; Kohjiya, S. *Chem. Phys. Lett.* **1998**, *287*, 342.
(23) Sarkar, M. D.; Urayama, K.; Kawamura, T.; Kohjiya, S. *Liq. Cryst.* **2000**, *27*, 795.
(24) Shivaev, V. P.; Kostromin, S. G.; Plate, N. A. *Eur. Polym. J.* **1982**, *18*, 651.
(25) Portugall, M.; Ringsdorf, H.; Zentel, R. *Makromol. Chem.* **1982**, *183*, 2311.
(26) Benmouna, F.; Ruhe, J.; Johannsmann, D. *Liq. Cryst.* **1999**, *26*, 1655.
(27) Nwabunma, D.; Kyu, T. *Macromolecules* **1999**, *32*, 664.
(28) Chandrasekhar, S. *Liquid Crystals*, 2nd ed.; Cambridge University Press: Cambridge, 1992.
(29) de Gennes, P.-G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Oxford: New York, 1993.

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