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Volume Transition of Liquid Crystalline Gels in Isotropic Solvents

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ABSTRACT: The equilibrium swelling and phase behavior of the side chain liquid crystalline (LC) networks in isotropic (nonmesomorphic) solvents has been investigated as a function of temperature. The LC networks swollen in di-*n*-amyl phthalate or di-*n*-butyl phthalate exhibit discontinuous volume transition driven by nematic ordering: The swollen isotropic gel is discontinuously transformed into the shrunken nematic gel at a characteristic temperature ($T_{\mathrm{NI}}{}^{\mathrm{G}}$). The transition temperature $T_{\mathrm{NI}}{}^{\mathrm{G}}$ depends on the swelling solvent, and $T_{\mathrm{NI}}{}^{\mathrm{G}}$ decreases as the degree of equilibrium swelling in the isotropic phase increases. The volume transition phenomena observed are satisfactorily described by a mean field theory for nematic gel.

Introduction

It has been reported that some polymer gels undergo a discrete and reversible volume change with an infinitesimal change in temperature, solvent composition, pH, etc.[1] These volume transition phenomena of polymer gels have attracted much interest because of their potential applications as actuator, drag delivery system, etc.[2] Recently, we reported that liquid crystalline (LC) networks swollen in nematic solvents exhibited a volume transition driven by nematic−isotropic phase transition of the LC molecules inside the gel:[3−5] The swollen isotropic gel was discontinuously transformed into the shrunken nematic gel. The volume transition of the nematic gels is induced by nematic (orientational) ordering, which is drastically different from the known volume transition phenomena of isotropic gels triggered by the balance between the repulsive and attractive molecular forces on the network chains such as van der Waals, hydrophobic, ionic, and hydrogen bonding.[1] Equilibrium swelling behavior of nematic gels in nematic solvents is strongly correlated with the LC phases inside and outside the gels, which suggests that the swelling of nematic gels in nematic solvents is mainly governed by nematic order of each LC molecule. The correlation of the equilibrium swelling and the LC phases observed is successfully described by a mean field theory for nematic gel.[4−7] The volume transition phenomena of the LC gels in nematic solvents yield a simple question: Do the LC networks also exhibit a volume transition in isotropic (nonnematogenic) solvents? The mean field theory for nematic gel predicts that in isotropic solvent, nematic ordering yields the condensation of the gel, i.e., the collapse of the gel.[8−10] In contrast, there exists no experimental study to elucidate quantitatively the correlation between swelling and phase behavior for nematic gel in isotropic solvent. Kishi et al.[11] reported that a poly(γ-benzyl L-glutamate) gel showed a large volume change resulting from the cholesteric−isotropic transition when a composition of a mixture of isotropic solvents was used as a variable. In their study,[11] however, it was not clear whether the volume change at the cholesteric−isotropic transition was discontinuous or not. In the present study, the equilibrium swelling and phase properties of nematic networks in isotropic solvents are investigated especially in the vicinity of the nematic−isotropic transition temperatures. It is demonstrated that a discontinuous transition in gel volume induced by nematic ordering takes place in conventional isotropic solvents. This finding is of significance to understand the role of nematic ordering in the swelling behavior of LC gels. The experimental data are compared with the prediction of the mean field theory for nematic gel. The coupling phenomena between rubber elasticity and nematicity in dry thermotropic LC elastomers have received much attention during recent years owing to the applicability to artificial muscles,[12,13] actuators,[14] electrooptical and opto-mechanical devices,[15,16] and damping materials.[17] The sharp volume transition phenomena of thermotropic LC gels in conventional isotropic solvents accompanying nematic−isotropic transition will extend further the applicability to interesting industrial devices.

Mean Field Theory for Nematic Network in Isotropic Solvent

The outline of the mean field theory[8,9] for nematic network in isotropic solvent is described here. Neither the dangling mesogen−backbone polymer interaction nor the effect of totally nonmesomorphic backbone on solubility specific to side chain LC networks is explicitly considered in the theory, because the former and the latter are reflected in the nematic−isotropic transition temperature observed and the Flory−Huggins mixing interaction parameter, respectively.[18,19] The experimental phase diagrams for some un-cross-linked side chain LC polymers are successfully described by a mean field theory along the same lines.[18,19]

We denote by ϕ the volume fraction of the network, and the degree of swelling Q is given by the inverse of ϕ:

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$$\phi = \frac{V_0}{V} = \frac{1}{Q} = \frac{b^3 n N_{\rm g}}{b^3 N_{\rm t}} \qquad (1)$$

where V_0 and V are the gel volumes in the dry and fully swollen states, respectively, b^3 is the volume of an unit segment or a solvent molecule. The total number of unit cells inside the gel ($N_{\rm t}$) is given by $N_{\rm t} = nN_{\rm g} + N_0$ where $N_{\rm g}$ and N_0 are the numbers of the network chains and solvents inside the gel, respectively. The number of the segments on a network chain (n) comprising mesogenic units and nonmesomorphic components is given by $n = (n_{\rm m} + n_{\rm s})\ t$ where $n_{\rm m}$ and $n_{\rm s}$ are the numbers of sites (segments) occupied by a mesogen and a nonmesomorphic unit (spacer), respectively, and t is the number of a repeating unit.

It is assumed here that the total free energy *per lattice site* is written as a sum of three contributions:

$$f = f_{\rm el} + f_{\rm mix} + f_{\rm nem} \qquad (2)$$

where $f_{\rm el}$ is the elastic free energy of the nematic network, $f_{\rm mix}$ is the free energy of mixing of the network with the solvent, and $f_{\rm nem}$ is the free energy of nematic ordering.

On the basis of the Flory–Huggins theory,[20] $f_{\rm mix}$ may be expressed as

$$\frac{f_{\rm mix}}{k_{\rm B}T} = (1-\phi)\ln(1-\phi) + \chi\phi(1-\phi) \qquad (3)$$

where $k_{\rm B}$ is the Boltzmann constant, T is the absolute temperature, and χ is the Flory–Huggins parameter characterizing the mixing interactions between network and solvent. In this treatment, the interaction between spacer and mesogen in the network is not explicitly considered, and χ reflects the interaction of the overall network with the solvent.

The change of elastic free energy density of nematic network upon swelling was derived by Warner et al.[6,8,21]

$$\frac{f_{\rm el}}{k_{\rm B}T} = \frac{3}{2n}\left\{\left[\frac{\phi}{(1+2S)(1-S)^2}\right]^{1/3} + \frac{1}{3}\ln(1+2S)(1-S)^2\right\} \qquad (4)$$

where S is the nematic (orientational) order for mesogen of the network, and $S = 0$ yields the classical expression of $f_{\rm el}$ for isotropic network. The definition of S is given by

$$S = \int P_2\,(\cos\theta)\psi(\theta)\ {\rm d}\Omega \qquad (5)$$

where θ is the angle between the mesogen and the director, Ω is the solid angle, and $P_2(x) = (3x^2 - 1)/2$ is the second Legendre polynomial. The function $\psi(\theta)$ is the normalized orientation distribution function expressed by

$$\psi(\theta) = \frac{\exp[\eta P_2(\cos\theta)]}{\int \exp[\eta P_2(\cos\theta)]\ {\rm d}\Omega} \qquad (6)$$

where η is a dimensionless parameter characterizing the strength of the nematic field.

The nematic free energy per site $f_{\rm nem}$ may be given by the Maier–Saupe theory[22,23]

$$\frac{f_{\rm nem}}{k_{\rm B}T} = \frac{\phi_m}{n_m}\int \psi(\theta)\ln 4\pi\psi(\theta)\ {\rm d}\Omega - \frac{1}{2}\nu{\phi_{\rm m}}^2 S^2 \qquad (7)$$

where $\phi_{\rm m}$ is the volume fraction of mesogen given by $\phi_{\rm m} = \phi\ n_{\rm m}/(n_{\rm m} + n_{\rm s}) = \phi\ (1 - p)$ with the spacer fraction $p = n_{\rm s}/(n_{\rm m} + n_{\rm s})$. The parameter ν is the Maier–Saupe interaction parameter between the mesogens, and it is assumed to be inversely proportional to temperature.

The expression of η in terms of S is obtained via minimization of the free energy with respect to $\psi(\theta)$:

$$\eta = n_{\rm m}\nu\phi_{\rm m}S - \frac{3n_{\rm m}S}{n\phi_{\rm m}(1+2S)(1-S)}\left\{\left[\frac{\phi}{(1+2S)(1-S)^2}\right]^{1/3} - 1\right\} \qquad (8)$$

The equilibrium swelling is governed by equality of the chemical potentials of the solvents inside and outside the gel (designated as μ and $\mu°$, respectively):

$$\frac{\mu - \mu°}{k_{\rm B}T} = 0 \qquad (9)$$

The following equilibrium condition is obtained using $(\mu - \mu°)/(k_{\rm B}T) = f - \phi({\rm d}f/{\rm d}\phi)$:

$$\frac{1}{n}\left\{\left[\frac{\phi}{(1+2S)(1-S)^2}\right]^{1/3} + \frac{1}{2}\ln(1+2S)(1-S)^2\right\} + \ln(1-\phi) + \phi + \chi\phi^2 + \frac{1}{2}\nu S^2{\phi_{\rm m}}^2 = 0 \qquad (10)$$

The equilibrium values of ϕ (or Q) and S as a function of temperature can be calculated by solving eqs 5 and 10.

Experimental Section

Sample Preparation. The side chain LC networks were prepared by free radical copolymerization of the mesogenic acrylate monomer (Figure 1), styrene monomer, and 1,6-hexanediol diacrylate (cross-linker). 2,2′-Azobisisobutylnitrile was employed as initiator. The mesogenic acrylate monomer was synthesized after the method in the literature.[24] The network totally composed of the LC monomers (LCN-100/0) and the copolymeric network comprising the LC monomers and the styrene monomers (LCN-90/10) were prepared. In the latter case, the molar ratio of the LC monomer and styrene monomer during synthesis was 90:10. Each of the initiator and cross-linker concentrations in the total reactants was 1 mol % for both networks. The reactant mixtures were dissolved in toluene so that the total reactant concentration would be 3.27 × 10^{-3} mmol/μL for LCN-100/0 and LCN-90/10. The reactant mixtures were polymerized in capillaries with a diameter of several hundreds of micrometers at 80 °C where the LC monomer was in the isotropic phase. The resulting cylindrical gels were extracted from the capillaries, and immersed in toluene for 1 week to wash out the materials which were not incorporated into the networks. The toluene was renewed everyday. After the washing procedure, the gels were gradually deswollen in mixtures of toluene and methanol by increasing the methanol content stepwise. The fully deswollen gels were completely dried in air. The nematic–isotropic transition temperatures of LCN-100/0 and LCN-90/10 in the dry states were estimated as 125 and 117 °C in cooling process by polarized optical microscopy, respectively.

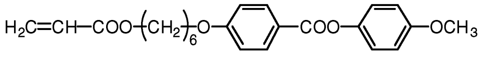


Figure 1. Molecular structure of the employed liquid crystalline monomer.

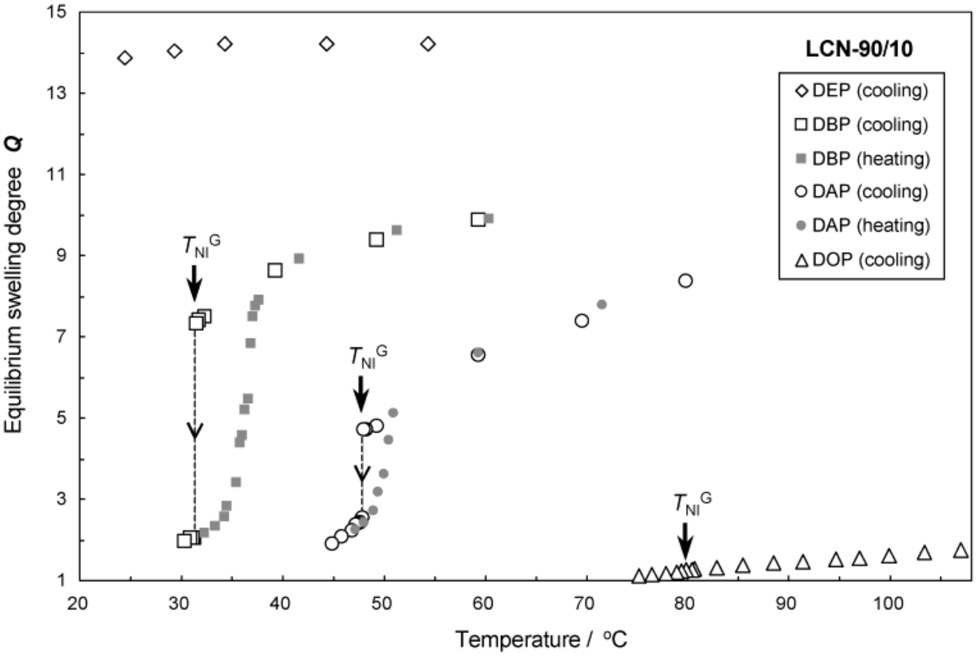
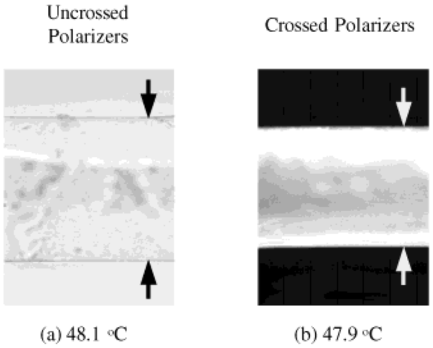


Figure 2. Temperature dependence of equilibrium swelling degree (Q) of LCN-90/10 in four different isotropic solvents, i.e., diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), di-*n*-amyl phthalate (DAP), and di-*n*-octyl phthalate (DOP). The nematic ordering of the gel takes place at T_{NI}^G: $T_{NI}^G = 31.3$, 47.9, and 79.8 °C for DBP, DAP, and DOP, respectively.

Swelling Measurement. The dry LC networks were allowed to swell in an optical cell by the di-*n*-alkyl phthalate homologues: diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), di-*n*-amyl phthalate (DAP), and di-*n*-octyl phthalate (DOP). The measurement of gel diameters and the phase observation were carried out as a function of temperature by a Nikon polarizing optical microscope E600 POL equipped with a Linkam LK-600PM sample stage under a nitrogen atmosphere.[3−5] The temperature was controlled with an accuracy of better than ±0.03 °C. In the beginning, the dry gel was allowed to swell in the solvent at a temperature where the swollen gel was in the isotropic phase. Swelling temperature was gradually reduced after confirming that the swelling equilibrium was achieved at each temperature. For the samples swollen in DBP and DAP, the swelling behavior in heating process was also examined after the measurement in cooling process. The swelling was isotropic throughout the measurements, and anisotropic swelling was not observed due to a polydomain nematic structure. Degree of equilibrium swelling (Q) was determined by the ratio of the gel diameters in the dry and swollen states (d_o and d_s, respectively) as $Q = V/V_o = (d_s/d_o)^3$ where V and V_o are the gel volumes in the swollen and dry states, respectively.

Results and Discussion

Figure 2 displays the degree of equilibrium swelling (Q) as a function of temperature for LCN-90/10 in each solvent, i.e, DEP, DBP, DAP, or DOP. Evidently, the swelling degree systematically varies with the number of carbon atoms in alkyl groups of the di-*n*-alkyl phthalate solvents (a): Q increases with decreasing a. In DOP with $a = 8$, Q remains small ($Q < 2$) over the whole temperature range examined. In DEP, DBP, and DAP with $a \leq 5$, the gel swells largely. Most interestingly, in DBP or DAP with a moderate a ($a = 4$ or 5), under cooling process, the swollen isotropic gel is discontinuously shrunken into the nematic state at a certain temperature (T_{NI}^G): $T_{NI}^G = 31.3$ and 47.9 °C for DBP and DAP, respectively. The discontinuity in volume change is obvious because the temperature gap between the swollen and shrunken phases is only 0.2 °C. Figure 3 shows the optical micrographs of the gel in DAP at 48.1 and 47.9 °C ($=T_{NI}^G$). The volume transition of LC gel driven by nematic ordering was first observed in nematic solvents.[3] The results here demonstrate that LC gel also exhibits a volume transition induced by nematic ordering in isotropic (nonmesomorphic) solvents. In DOP with $a = 8$, the gel undergoes the nematic−isotropic transition at 79.8 °C, but the gel volume is not significantly altered by the transition. The small magnitude of swelling in DOP ($Q = 1.25$ at T_{NI}^G) masks the discontinuous volume change by nematic ordering. It is found that T_{NI}^G depends on the solvent; T_{NI}^G decreases as Q (i.e., the amount of solvent inside the gel) in the isotropic phase increases. It should also be noted that the T_{NI}^G values in the swollen state are much lower than the nematic−isotropic transition temperature of the network in the dry state (117 °C). This results from that the nematicity of the swollen network is diluted by the isotropic solvent inside the gel. In the temperature range examined, the gel in DEP with $a = 2$ remains isotropic, and no nematic−isotropic transition



(a) 48.1 °C (b) 47.9 °C

Figure 3. Optical micrographs for the cylindrical liquid crystalline gel LCN-90/10 in DAP. The pictures represent (a) swollen isotropic phase at 48.1 °C ($= T_{NI}^G + 0.2$ °C) and the (b) nematic shrunken phase at 47.9 °C ($= T_{NI}^G$). The micrographs show that a discontinuous decrease in gel diameter takes place at T_{NI}^G as a result of nematic ordering. Arrows indicate the boundary of the gel surface.

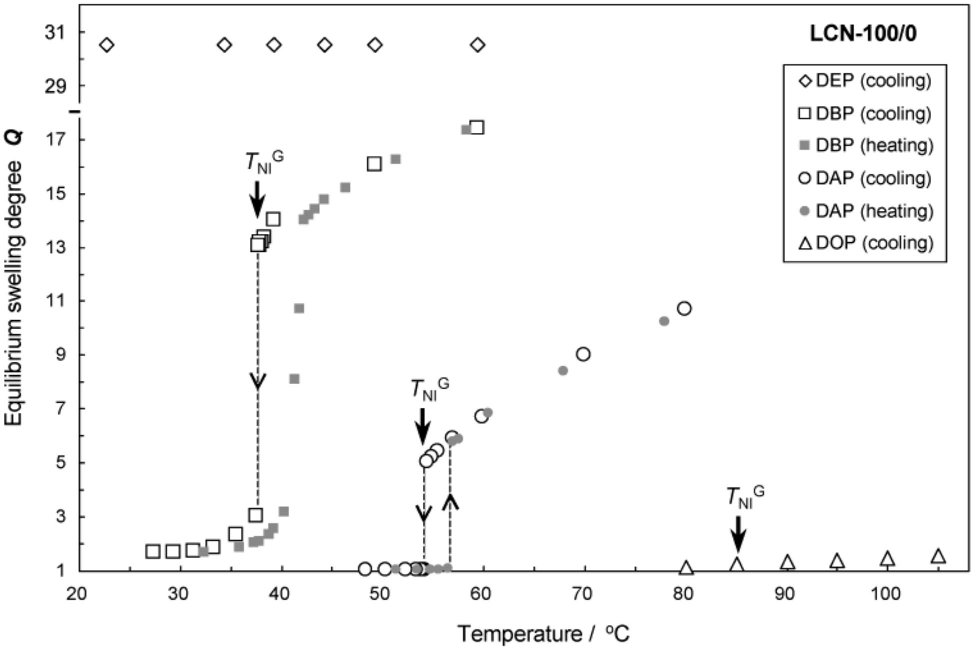
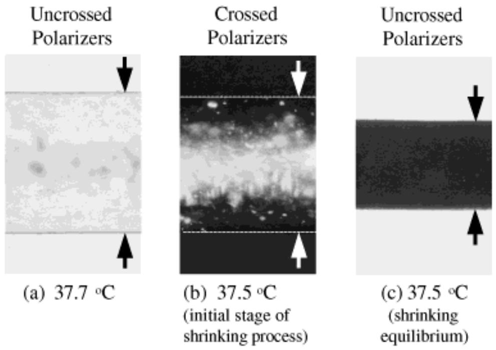


Figure 4. Temperature dependence of equilibrium swelling degree (Q) of LCN-100/0 in four different isotropic solvents, i.e., diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), di-*n*-amyl phthalate (DAP), and di-*n*-octyl phthalate (DOP). The nematic ordering of the gel takes place at T_{NI}^{G}: T_{NI}^{G} = 37.5, 54.2, and 85.0 °C for DBP, DAP, and DOP, respectively.

is observed. This is due to the high degree of swelling ($Q \approx 14$), and T_{NI}^{G} in DEP is expected to exist below the room temperature.

The swelling behavior in heating process was also investigated for LCN-90/10 in DBP and DAP. As can be seen in Figure 2, both systems show appreciable thermal hysteresis in the swelling and phase behavior. The transition temperature in heating process is shifted to higher temperature region in comparison with that in cooling process. Further, the nematic–isotropic transition upon heating is broadened: The bright appearance of the gel under cross-polarized condition becomes dark gradually over the finite temperature range 33 °C < T < 42 °C in DBP or 49 °C < T < 52 °C in DAP. In addition, the resulting volume increase also proceeds continuously. These results are in contrast to no significant thermal hysteresis in the swelling and phase behavior for the nematic gels in nematogenic solvents.[3,4] The shift of the transition temperature may not be surprising because the volume transition triggered by nematic–isotropic transition is originally classified into the first-order phase transition. However, the reason for the broadening of the nematic–isotropic transition is not clear at present. The broad transition in heating process observed is apparently similar to the melting of the polymer crystallites with a finite distribution in crystallite size which takes place over a finite temperature range. The nematic phase of the gel formed in the isotropic solvents may be composed of the polydomain structure with a relatively broad distribution in the size of nematic domain.

Figure 4 displays Q as a function of T for LCN-100/0 in each solvent, DEP, DBP, DAP, or DOP. The dependence of the swelling behavior on the solvent is qualitatively similar to that for LCN-90/10. In DBP or DAP under a cooling process, a discontinuous volume decrease triggered by nematic ordering occurs at a characteristic temperature: T_{NI}^{G} = 37.5 °C for DBP; T_{NI}^{G} = 54.2 °C for DAP. In the initial stage of the shrinking process of LCN-100/0 in DBP or DAP at T_{NI}^{G}, an indication of nematic ordering is observed; in the later stage, the appearance under cross-polarized condition becomes dark as the shrinking proceeds. The fully shrunken gel shows the opaque appearance but without the definite nematic texture, which is unchanged for at least 1 month after the shrinking equilibrium is achieved. The optical micrographs in the corresponding stages are shown in Figure 5. In DOP, the similar transition from the transparent gel into the opaque one is also observed at T_{NI}^{G} = 85.0 °C, although the resulting volume change is not appreciable due to the small degree of swelling (Q = 1.26 at T_{NI}^{G}). As in the case of LCN-90/10, in the temperature range examined, LCN-100/0 in DEP exhibits no volume transition due to the highly diluted nematicity by the high degree of swelling ($Q \approx 31$). In each solvent, T_{NI}^{G} of LCN-100/0 is slightly higher but



(a) 37.7 °C (b) 37.5 °C (initial stage of shrinking process) (c) 37.5 °C (shrinking equilibrium)

Figure 5. Optical micrographs for the cylindrical liquid crystalline gel LCN-100/0 in DBP. The pictures represent (a) the equilibrium swollen isotropic phase at 37.7 °C (=T_{NI}^{G} + 0.2 °C), (b) the initial stage of the shrinking process at 37.5 °C (=T_{NI}^{G}), and (c) the equilibrium shrunken phase at T_{NI}^{G}. The micrograph (b) shows the indication of nematic ordering inside the gel at the initial stage of the shrinking (12 h after). The appearance of the gel at T_{NI}^{G} under cross-polarized condition becomes dark as the shrinking proceeds. In the shrinking equilibrium (14 days after), the gel exhibits the opaque appearance but without definite nematic texture as shown in part c. The arrows in parts a–c and the dotted white lines in part b indicate the boundary of the gel surface.

comparable to that of LCN-90/10. The comparison is not simple, because T_{NI}^G is a function of the original network nematicity as well as the degree of swelling.

LCN-100/0 in DBP or DAP exhibiting a sharp volume transition in cooling process shows a considerable thermal hysteresis as in the case of LCN-90/10. In heating process, the shrunken gel starts to swell at a temperature definitely above T_{NI}^G in cooling process; in DBP, the change from the shrunken phase to the swollen phase occurs continuously over the temperature range 38 °C $< T <$ 42 °C; in DAP, the volume transition in the heating process takes place sharply at 57.0 °C within a range of 0.5 °C.

The temperature T_{NI}^G in DAP is much lower than T_{NI}^N (=125 °C) but somewhat higher than T_g (ca. 30 °C) where T_{NI}^N and T_g are the nematic−isotropic transition temperature and the glass transition temperature of the dry LCN-100/0, respectively. From this thermodynamic viewpoint, the shrunken gel in DAP with $Q = 1.05$ corresponding to almost the dry state should form the nematic phase. The opaque appearance but without appreciable nematic texture in the shrunken state will be due to a metastable structure frozen in the course of the transition from the swollen isotropic phase to the shrunken nematic phase. The sharp volume increase in DAP upon heating indicates that the shrunken network is not in the glassy state but substantially in the rubbery state; the metastable structure does not result from the glass-forming effect. The glass-forming effect is also ruled out for the shrunken LCN-100/0 in DBP due to the high solvent content (>50 vol %) which is sufficient to plasticize the network. Unlike the nematic−isotropic transition of the dry LC networks, the nematic ordering of the swollen LC networks is accompanied by a large decrease in gel volume due to the loss of the solvent. In the transition accompanied by a large shrinkage, the high density of mesogen in LCN-100/0 (totally composed of the LC monomers) may tend to stabilize a metastable structure in the course of the transformation into the shrunken nematic phase. It should be recalled that LCN-90/10 with a lower mesogen density forms the definite nematic phase in the equilibrium shrunken state.

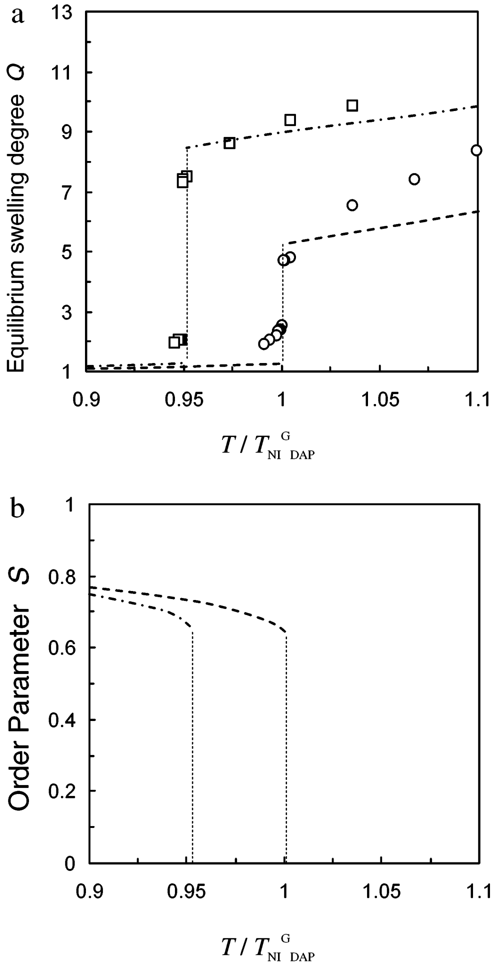


Figure 6. (a) Comparison of the swelling-temperature data for LCN-90/10 in DBP and DAP under cooling process with the prediction of the mean field theory. The absolute temperature (T) in the figure is reduced by the nematic−isotropic transition temperature in DAP ($T_{NI}^G = 320.9$ K). The broken line and the dotted broken line represent the fitted theoretical swelling curves for the data in DAP and DBP, respectively. The identical parameter set related to gel structure is used for the data-fit in DAP and DBP: $n = 300$, $n_m = 2.75$, and $p = 0.154$. The fitted parameter concerning the isotropic mixing ($\chi = \chi_1/T + \chi_2/T^2$) is altered as $\chi_{DBP}/\chi_{DAP} = 0.79$: $\chi_1/\nu = 0.19$, $\chi_2/\nu = -0.0475$ for DAP; $\chi_1/\nu = 0.15$, $\chi_2/\nu = -0.0375$ for DBP. (b) Theoretical orientational order parameters as a function of the reduced temperature calculated with the same parameter values as part a.

Part a of Figure 6 illustrates the comparison of the swelling data for LCN-90/10 in DBP and DAP under cooling process with the prediction of the mean field theory. The data of LCN-90/10 exhibiting the definite nematic phase in the shrunken state were employed for the test of the theory. The absolute temperature in the figure is reduced by T_{NI}^G in DAP. Part b of Figure 6 shows the orientational order parameter S as a function of the reduced temperature obtained simultaneously in the data fit. In the data fit for the gels in DBP and DAP, the identical parameter set related to the gel structure ($n = 300$, $n_m = 2.75$, $p = 0.154$) was used, while the smaller χ value was employed for the data for DBP relative to that for DAP as $\chi_{DBP}/\chi_{DAP} = 0.79$. To reproduce the fairly strong T dependence of Q in the isotropic phase observed, it was required to introduce the quadratic term of $1/T$ into the T dependence of χ as $\chi = \chi_1/T + \chi_2/T^2$. The fitted values are $\chi_1/\nu = 0.19$, $\chi_2/\nu = -0.0475$ for DAP and $\chi_1/\nu = 0.15$, $\chi_2/\nu = -0.0375$ for DBP. The degree of swelling in the isotropic phase is governed by the magnitude of χ. As χ becomes smaller, Q in the isotropic phase becomes larger. The theory well demonstrates that the nematic ordering of gel (i.e., a jump of S) induces a discontinuous decrease in gel volume; the difference of T_{NI}^G in DBP and DAP is primarily due to the difference in χ. This supports the aforementioned interpretation for the difference of T_{NI}^G in DAP and DBP on the basis of the dilution effect of the solvent on the nematicity of gel. Meanwhile, there exists an appreciable difference in the experimental and theoretical values of Q in the shrunken nematic phase. In the experiment, the gel largely shrinks as a result of nematic ordering, but the nematic gel still exhibits a finite swelling, i.e., $Q \approx 2$ in DBP and DAP. The theoretical value of Q in the nematic phase is almost unity, which is not appreciably influenced by the χ value: The theory predicts that the nematic ordering expels nearly all the amount of solvent from the gel. The theory assumes the formation of nematic monodomain structure with globally unique orientation, while the nematic gels in the present study form the polydomain structure. A finite swelling of the nematic gels may originate from the nematic polydomain structure with locally highly ordered orientation but globally random orientation. A swelling experiment under an external field to yield the monodomain structure will reveal this issue, which is a future subject of our study.

Summary

The side chain LC networks swollen in the isotropic solvent (DAP or DBP) exhibit a discontinuous large decrease in gel volume accompanying the nematic ordering: Upon cooling, the swollen isotropic gel discontinuously changes into the shrunken nematic gel at a characteristic temperature (T_{NI}^{G}). The transition temperature T_{NI}^{G} is altered by the solvent, and T_{NI}^{G} primarily depends on the degree of swelling, i.e., the degree of dilution of network nematicity. As the swelling degree in the isotropic phase increases, T_{NI}^{G} decreases. The volume transition phenomena observed are well accounted for using a mean field theory for nematic gel. The definite nematic phase is observed in the equilibrium shrunken state for the LC network containing a small amount of styrene units (10 mol %) in the backbone. Meanwhile, the pure LC network totally composed of the LC monomers exhibits an opaque appearance but without definite nematic texture in the fully shrunken state, while in the initial stage of the shrinking process, the indication of the nematic ordering appears. The structure without definite nematic alignment in the shrunken state will be a metastable structure frozen in the course of the transition from the isotropic swollen state to the nematic shrunken state due to the high density of mesogen in the pure LC network.

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