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Volume Phase Transition of Monodomain Nematic Polymer Networks in Isotropic Solvents Accompanied by Anisotropic Shape Variation

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ABSTRACT: The equilibrium swelling and phase behavior of monodomain nematic networks in nonmesomorphic solvents have been investigated as a function of temperature. The gels thermoreversibly undergo a phase transition between the swollen isotropic and shrunken monodomain nematic states with accompanying an anisotropic shape change. The nematic ordering occurs continuously within a narrow temperature range, which induces a significant reduction in gel volume as well as an elongation in the director direction. The length of the gels along the director axis in the nematic phase becomes larger than that in the isotropic phase, despite a considerable volume decrease upon nematic ordering. As temperature decreases, the shape anisotropy of the nematic gels increases without appreciable volume change, and becomes almost constant at the sufficiently low temperatures. A theory is proposed to describe the anisotropic swelling and phase equilibria of the monodomain nematic networks in isotropic solvents. The theory successfully describes the features of the swelling behavior observed.

Introduction

Liquid crystalline polymer networks have received much interest of scientists, because the hybrid character exhibiting the properties of both polymer networks and liquid crystals yields a wealth of new interesting phenomena.[1,2] We found that the nematic networks swollen in nonmesomorphic[3] or nematic solvents[4−6] thermoreversibly undergo a volume phase transition induced by the nematic−isotropic (N−I) transition, i.e., a phase transition between the swollen isotropic and shrunken nematic states. The time course of the volume transition in the nematic gels obeys an interesting kinetics because of the coupling of the diffusion of polymer networks with the N−I transition.[7] The nematic networks in the previous studies[3−7] were prepared by cross-linking mesogenic monomers in the isotropic phase, so that the nematic phase showed a polydomain texture where the director directions of the constituent nematic domains are globally random. Such polydomain nematic gels exhibit no anisotropy in swelling due to the absence of macroscopic director orientation. To cross-link mesogenic monomers or polymers in the macroscopically aligned nematic state offers a monodomain nematic network with global director orientation.[8−14] The monodomain nematic networks in the dry state show a spontaneous elongation parallel to the director axis upon nematic ordering,[8−14] indicating that the appearance of global director orientation causes anisotropic deformations of the networks. Their studies[8−14] focused on the N−I transition and the resulting shape change in “dry” monodomain nematic networks without appreciable volume change.

In the present study, we investigate the volume transition of the side chain monodomain nematic networks swollen in isotropic solvents. We demonstrate that the monodomain nematic gels exhibit a large volume change as well as an anisotropic shape variation at the N−I transition. This finding will also develop further the applicability of nematic gels to the industrial devices. The anisotropic swelling of some monodomain nematic networks was observed by several researchers,[15,16] but the temperature-swelling phase diagrams across the N−I transition for isotropic solvent systems have not yet been studied experimentally. In addition, no attempt was made in their studies[15,16] to interpret the anisotropic swelling behavior theoretically. There exist some theoretical studies[17,18] on the swelling of nematic networks in isotropic solvents. In the present study, we compare the experimental data with the prediction of a model along the line of the earlier theories.[17,18]

Theory for Anisotropic Swelling of Nematic Networks in Isotropic Solvents

In this section, we describe the mean field theory for the swelling of nematic networks whose cross-links are introduced in the *nematic* phase in accordance with the condition of our experiments. The framework of the present theory is along the same line of the earlier theories[17,18] on the swelling-temperature phase diagrams of nematic networks formed in the *isotropic* phase. As pointed out in ref 2, within the framework of the theory concerned, the characteristics such as spontaneous shape variations in the theoretical prediction are unaffected by whether the network is formed in the isotropic or nematic phase.

The present theory does not consider explicitly the interactions specific to side chain nematic networks such as the dangling mesogen-backbone polymer interaction and the effect of totally nonmesomorphic backbone on solubility. The former interaction is reflected in the N−I transition temperature observed, and the latter effect is included in the Flory−Huggins mixing interaction parameter. The orientational order parameters for the chain backbone (S_B) and the dangling mesogen (S) differ in general, but they can be connected through a proportional constant.[2] For simplicity, $S_B = S$ is assumed here. The experimental phase diagrams for the solutions of un-cross-linked side chain nematic polymers are successfully explained by a mean field approach on the basis of the same treatments.[19,20]

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Let us consider the nematic network where each network chain is composed of mesogenic and nonmesomorphic monomers with the axial ratios n_m and n_s, respectively. The axial ratios correspond to the numbers of sites occupied by the monomers. The number of the segments (sites) on a single network chain (n) is given by $n = (n_m + n_s)t$ where t is the number of the repeating units. The degree of swelling Q_0 for a network in an isotropic solvent with the axial ratio of unity is defined as the ratio of the gel volumes in the swollen and formation states of the network (V and V^0, respectively):

$$Q_0 = \frac{V}{V^0} = \frac{\phi^0}{\phi} = \frac{b^3(nN_g + N_s)}{b^3(nN_g + {N_s}^0)} \tag{1}$$

where ϕ, b^3, N_g, and N_s are the volume fraction of network, the volume of an unit segment or a solvent molecule, the number of the network chains, and the number of the solvent molecules inside the gel, respectively. The superscript 0 denotes the state of network formation. The anisotropic swelling of nematic networks with uniaxial orientation is characterized by the principal ratios λ_L and λ_T

$$Q_0 = \lambda_L {\lambda_T}^2 \tag{2}$$

where the subscripts L and T represent the axes parallel and perpendicular to the nematic director, respectively. The principal ratios λ_L and λ_T are defined by the ratios of the dimensions along each axis in the swollen and formation states.

The change of the total free energy density (i.e, free energy per lattice site) Δf is customarily written as a sum of those of the free energy densities stemming from elasticity of nematic network, isotropic mixing of network with solvent and nematic ordering of mesogenic molecules (designated as f_{el}, f_{mix}, and f_{nem}, respectively):[17,18]

$$\Delta f = \Delta f_{el} + \Delta f_{mix} + \Delta f_{nem} \tag{3}$$

The expression of Δf_{el} for the nematic networks formed in the nematic phase was derived by Warner et al.[2,17,21] as

$$\frac{\Delta f_{el}}{k_B T} = \frac{\phi}{2n}\left[{\lambda_L}^2\frac{l_L^0}{l_L} + 2{\lambda_T}^2\frac{l_T^0}{l_T} - 3 - \ln\left(\frac{l_L^0\, l_T^{0\,2}}{l_L {l_T}^2}\right)\right] \tag{4}$$

where k_B and T are the Boltzmann constant and absolute temperature, respectively, and l is the effective step length for anisotropic Gaussian coils in the freely jointed chain model. The spontaneous uniaxial elongation λ_L is obtained by minimizing Δf_{el} with respect to λ_L as

$$\lambda_L = \left(\frac{\phi^0}{\phi}\right)^{1/3}\left(\frac{l_L}{l_T}\frac{l_T^0}{l_L^0}\right)^{1/3} = \left(\frac{\phi^0}{\phi}\right)^{1/3}\left(\frac{1+2S}{1-S}\right)^{1/3}\left(\frac{1-S^0}{1+2S^0}\right)^{1/3} \tag{5}$$

where S and S^0 are the orientational order parameters of the chain backbone in the swollen and formation states, respectively. In eq 5, the relations $l_L/l_T = (1+2S)/(1-S)$ and $l_L^0/l_T^0 = (1 + 2S^0)/(1 - S^0)$ are employed.[2] Using eqs 4 and 5, we obtain the form of Δf_{el} as a function of ϕ and S as

$$\frac{\Delta f_{el}}{k_B T} = \frac{3\phi^0}{2n}\left[\left(\frac{\phi}{\phi^0}\right)^{1/3}\left(\frac{A^0}{A}\right)^{1/3} - \frac{\phi}{\phi^0} - \frac{\phi}{3\phi^0}\ln\left(\frac{A^0}{A}\right)\right] \tag{6a}$$

where

$$A = (1 + 2S)(1 - S)^2 \tag{6b}$$

$$A^0 = (1 + 2S^0)(1 - S^0)^2 \tag{6c}$$

The form of Δf_{el} for a nematic network formed in the isotropic state is given by putting $S^0 = 0$ in this equation.

According to the Flory–Huggins theory,[22] Δf_{mix} is written as

$$\frac{\Delta f_{mix}}{k_B T} = (1 - \phi)\ln(1 - \phi) + \chi\phi(1 - \phi) \tag{7}$$

where χ is the Flory–Huggins parameter representing the mixing interaction between network and solvent, respectively.

The expression of Δf_{nem} based on the Maier–Saupe theory[23,24] is given by

$$\frac{\Delta f_{nem}}{k_B T} = \frac{\phi_m}{n_m}\int \psi(\theta)\ln[4\pi\psi(\theta)]\,d\Omega - \frac{1}{2}\nu{\phi_m}^2 S^2 \tag{8}$$

where 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 $p = n_s/(n_m + n_s)$. The parameter ν is the Maier–Saupe interaction parameter between the mesogens, and assumed to be proportional to reciprocal temperature. The orientation distribution function $\psi(\theta)$ is related to S as

$$S = \int P_2(\cos\theta)\psi(\theta)\,d\Omega \tag{9}$$

where θ is the angle between the chain backbone 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 expressed by

$$\psi(\theta) = \frac{1}{Z}\exp[\eta P_2(\cos\theta)] \tag{10}$$

where η is a dimensionless parameter characterizing the strength of the nematic field, and $Z = \int\exp[\eta P_2(\cos\theta)]\,d\Omega$ is the partition function to normalize $\psi(\theta)$. By minimizing the total free energy with respect to $\psi(\theta)$, the expression of η in terms of S and ϕ is obtained as

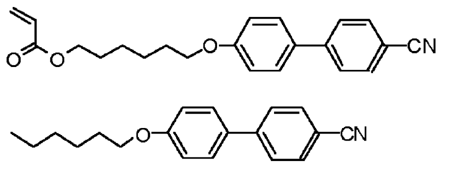
$$\eta = n_m\nu\phi_m S - \frac{3n_m\phi^0 S(1 - S)}{n\phi_m A}\left[\left(\frac{\phi A^0}{\phi^0 A}\right)^{1/3} - \frac{\phi}{\phi^0}\right] \tag{11}$$

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

$$\frac{\mu - \mu°}{k_B T} = 0 \tag{12}$$

Equation 12 yields the condition for equilibrium swelling:

$$\frac{\phi^0}{n}\left(\frac{\phi A^0}{\phi^0 A}\right)^{1/3} + \ln(1 - \phi) + \phi + \chi\phi^2 + \frac{1}{2}\nu{\phi_m}^2 S^2 = 0 \tag{13}$$



A-6OCB

6OCB

Figure 1. Molecular structures of the acrylate mesogenic monomer A-6OCB and the miscible nonreactive nematic solvent 6OCB.

The values of ϕ and S at a certain T in swelling equilibrium are obtained as the solutions satisfying eqs 9 and 13 simultaneously. The principal ratios λ_L and λ_T are calculated from eqs 2 and 5 with the corresponding values of ϕ and S. The reference state for λ_L (i.e., $\lambda_L = 1$) corresponds to the nematic phase with f^0 and S^0 where the network is formed. From the viewpoint of experiments, the principal ratio $\lambda_{||}$ measured from the dry state in the isotropic phase is more easily obtainable rather than λ_L:

$$\lambda_{||} = \frac{\lambda_L}{\lambda_L^0} = \frac{1}{\phi^{1/3}}\left(\frac{1+2S}{1-S}\right)^{1/3} \tag{14}$$

where $\lambda_L{}^0 = [f^0(1-S^0)/(1+2S^0)]^{1/3}$ is the value of λ_L in the dry isotropic state with $S = 0$ and $\phi = 1$. The corresponding principal ratio normal to the director $\lambda_\perp$ and swelling degree Q are written as

$$\lambda_\perp = \frac{1}{\phi^{1/3}}\left(\frac{1-S}{1+2S}\right)^{1/6} \tag{15}$$

and

$$Q = \frac{1}{\phi} = \lambda_{||}\lambda_\perp{}^2 \tag{16}$$

The ratio $\alpha = \lambda_{||}/\lambda_\perp$ is a measure for shape anisotropy of networks:

$$\alpha = \frac{\lambda_{||}}{\lambda_\perp} = \left(\frac{1+2S}{1-S}\right)^{1/2} \tag{17}$$

It should be noticed that when the dry isotropic state is taken as the reference state to measure the swelling, the resulting principal ratios, swelling degree and shape anisotropy ($\lambda_{||}$, $\lambda_\perp$, Q, and α) are apparently free from the parameters regarding the state of network formation (S^0 and f^0), unlike λ_L, λ_T, and Q_0 each of which is measured from the formation state.

Experimental Section

Sample Preparation. A mixture of the acrylate mesogenic monomer A-6OCB and the miscible nonreactive nematogen 4-*n*-hexyloxy-4′-cyanobiphenyl (6OCB) with the molar ratio of 50:50 was employed to prepare the monodomain nematic networks. The molecular structures of A-6OCB and 6OCB are shown in Figure 1. A-6OCB was synthesized according to the method in the literature,[25] and 6OCB purchased from Sigma-Aldrich was used without further purification. The N−I transition temperatures of A-6OCB and 6OCB were measured to be 48 and 76 °C by polarizing microscopy, respectively, but the transition temperature of A-6OCB involves some uncertainty due to the crystallization around the temperature concerned. 6OCB was mixed with A-6OCB to broaden the temperature range of the nematic phase.[26] Irgacure-784 kindly supplied from Ciba Specialty Chemicals and 1,6-hexanediol diacrylate were used as photoinitiator and cross-linker, respectively. The concentrations of the initiator and cross-linker were 0.5 and 7 mol % in the total reactants.

The reactant mixture was sandwiched between two glass plates separated by the spacers of 25 μm thickness. The plates were coated with the unidirectionally rubbed polyimide layer so that a homogeneous alignment of the nematic molecules could be achieved. The photopolymerization was carried out at 45 °C in the monodomain nematic phase of the mixture. The cell was irradiated using a xenon lamp with emission at a wavelength 526 nm for 15 min. The resulting gel film was separated from the glass plates, and allowed to swell in dichloromethane to wash out the unreacted materials as well as the nonreactive nematogen 6OCB. The swollen gel was gradually deswollen in the mixtures of dichloromethane and methanol by increasing the methanol content stepwise. The dry network, obtained by drying the fully deswollen network, shows the N−I transition at 107 °C upon cooling. The cross-polarizing microscopy confirmed a monodomain nematic texture in the dry network: The uniform birefringence was observed upon rotating the sample at a 45° position with respect to the analyzer.

Swelling Measurement. The small specimen with an area of ca. 0.5 mm × 0.5 mm cut out from the dry network film was employed to shorten the time needed for achieving the equilibrium swelling at each temperature. The specimen was allowed to swell in an optical cell by di-*n*-butyl phthalate (DBP) or di-*n*-amyl phthalate (DAP). The measurements of the dimensions of the gel and the phase observation were carried out as a function of temperature by a Nikon polarizing optical microscope E600POL equipped with a Linkam LK-600PM sample stage under a nitrogen atmosphere. The initial swelling temperature was 50 or 60 °C in the DBP or DAP system, respectively, where the swollen gel was in the isotropic phase. The swelling temperature was stepwise decreased after confirming that the swelling was equilibrated at each temperature. The swelling behavior in the heating process was also investigated in the same way after finishing the measurements in the cooling process. The swelling was anisotropic at temperatures in the nematic phase, and the anisotropic swelling was characterized by the principal ratios $\lambda_{||}$ and $\lambda_\perp$:

$$\lambda_{||} = d_{||}/d_{||,\mathrm{dry}}{}^{\mathrm{I}} \tag{18a}$$

$$\lambda_\perp = d_\perp/d_{\perp,\mathrm{dry}}{}^{\mathrm{I}} \tag{18b}$$

where the subscripts $||$ and $\perp$ denote the directions along and normal to the director axis, respectively, $d_{||,\mathrm{dry}}{}^{\mathrm{I}}$ and $d_{\perp,\mathrm{dry}}{}^{\mathrm{I}}$ are the dimensions in the corresponding directions of the dry isotropic network. The changes of $d_{||,\mathrm{dry}}{}^{\mathrm{I}}$ and $d_{\perp,\mathrm{dry}}{}^{\mathrm{I}}$ in response to temperature variation were negligibly small (less than 1%) in the isotropic phase. The equilibrium degree of swelling Q was calculated by eq 16 ($Q = \lambda_{||}\lambda_\perp{}^2$) assuming that the principal ratio in the thickness direction is equivalent to $\lambda_\perp$ (i.e., uniaxial orientation), although the network formation in the presence of cell walls may yield a slight deviation from uniaxial orientation.

Results and Discussion

Part a of Figures 2 and 3 illustrates the temperature (T) dependence of Q, $\lambda_{||}$, and $\lambda_\perp$ for the monodomain nematic network in DBP and DAP, respectively. The characteristics of the swelling and phase behavior for the two systems are substantially the same excepting the N−I transition temperatures and the swelling degrees. The descriptions below are common to the two systems unless specified otherwise. Upon cooling, the swollen isotropic gel continuously changes into the shrunken monodomain nematic gel around 29 °C in DBP or 44 °C in DAP within a narrow temperature range. Figure 4 displays the optical micrographs of the gel in DBP in the isotropic and nematic phases. The photographs indicate the formation of the monodomain

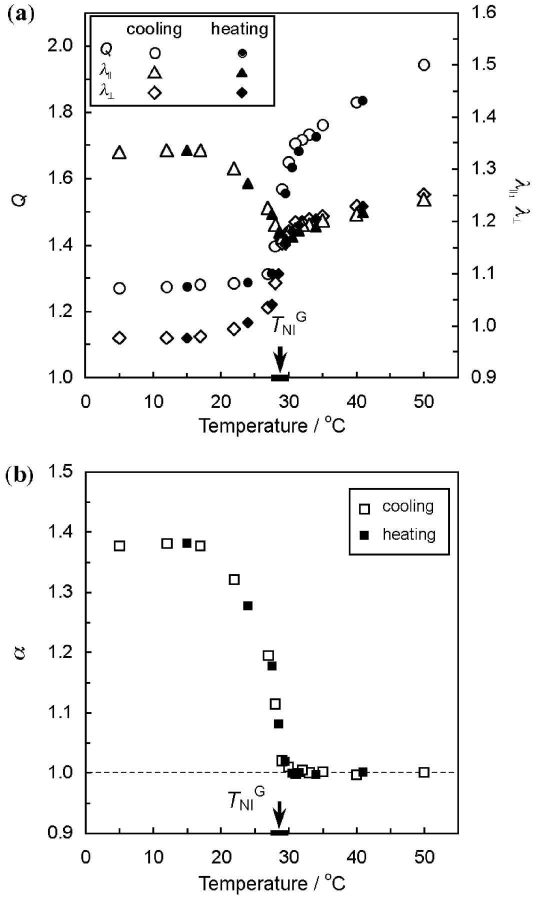


Figure 2. (a) Temperature dependence of the swelling degree (*Q*) and the principal ratios in the directions parallel and perpendicular to the nematic director ($\lambda_{\parallel}$ and $\lambda_{\perp}$, respectively) in the equilibrium swollen state of the monodomain nematic network in di-*n*-butyl phthalate (DBP). The gel exhibits a smooth phase transition between the isotropic swollen and nematic shrunken states around 29 °C. No significant difference in the swelling and phase behavior is present between the cooling and heating processes. (b) Temperature dependence of the ratio $\alpha = \lambda_{\parallel}/\lambda_{\perp}$ indicating the degree of shape anisotropy.

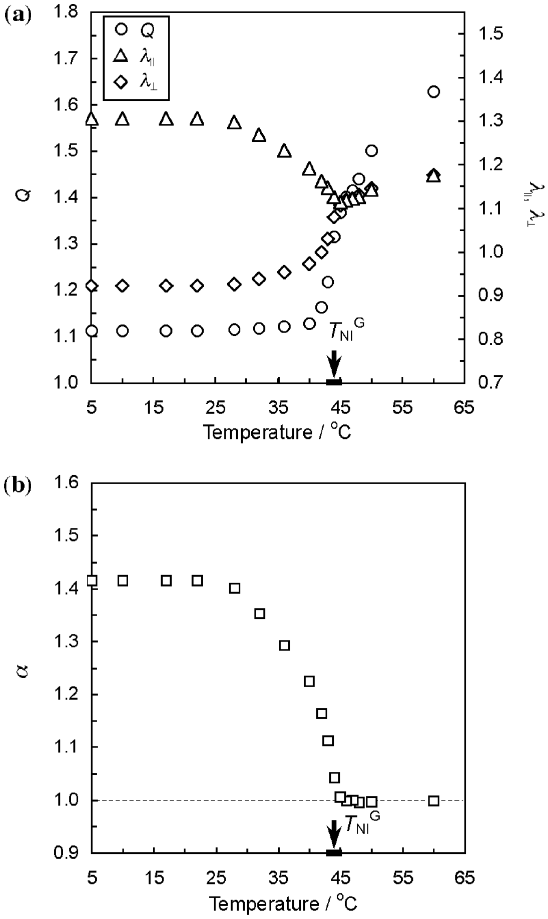
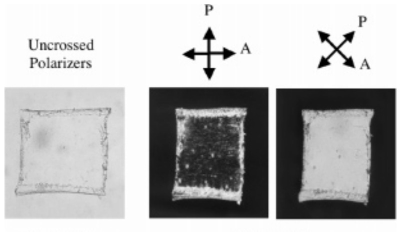


Figure 3. (a) Temperature dependence of the swelling degree (*Q*) and the principal ratios in the directions parallel and perpendicular to the nematic director ($\lambda_{\parallel}$ and $\lambda_{\perp}$, respectively) in the equilibrium swollen state of the monodomain nematic network in di-*n*-amyl phthalate (DAP). The gel exhibits a smooth phase transition between the isotropic swollen state and the nematic shrunken state around 44 °C. (b) Temperature dependence of the ratio $\alpha = \lambda_{\parallel}/\lambda_{\perp}$ indicating the degree of shape anisotropy.



(a) 50 °C (b) 12 °C

Figure 4. Optical micrographs of the monodomain nematic network swollen in di-*n*-butyl phthalate at (a) 50 °C in the isotropic phase and (b) 12 °C in the monodomain nematic phase. The arrow A or P denotes the optical axis of the analyzer or polarizer, respectively. The incomplete dark regions along the outline of the gel (left of Figure 4b) stem from the birefringence of the scratches formed unavoidably when cutting out the specimen from the dry network film.

nematic phase in the shrunken gel. The monodomain nematic phase does not appear distinctly at a definite temperature, but it becomes evident gradually within a narrow temperature range of ca. 2 °C coupled with a smooth volume change. The transition temperature T_{NI}^G in DBP is lower than that in DAP, resulting from the higher *Q* around T_{NI}^G in DBP: The dilution effect of the nonmesomorphic solvent on the original nematicity of the network increases with the solvent content inside the gel.

Of importance is that the volume decrease upon nematic ordering is accompanied by shape change with a considerable degree of anisotropy. Part b of Figures 2 and 3 shows the *T* dependence of the ratio $\alpha = \lambda_{\parallel}/\lambda_{\perp}$. The principal ratios $\lambda_{\parallel}$ and $\lambda_{\perp}$ in the isotropic phase are identical within experimental error as a result of isotropic swelling ($\alpha \approx 1$), whereas in the nematic phase $\lambda_{\parallel}$ is larger than $\lambda_{\perp}$ ($\alpha > 1$); i.e., the gel is elongated in the direction of nematic director. It is noteworthy that $\lambda_{\parallel}$ in the shrunken nematic phase is larger than that in the swollen isotropic phase, despite a volume reduction upon nematic ordering. Such a shape change caused by nematic ordering is also recognizable in Figure 4. The shape anisotropy of the nematic gel gradually increases with decreasing *T* without appreciable volume change, and α becomes a constant value (ca. 1.4 for both systems) at the temperatures more than 15 °C lower than T_{NI}^G.

The data obtained in the heating process are also displayed in Figure 2. No significant difference in the anisotropic swelling and phase behavior is observed between the cooling and heating processes, showing that the volume transition with the anisotropic shape change is thermoreversible. The global director orientation in

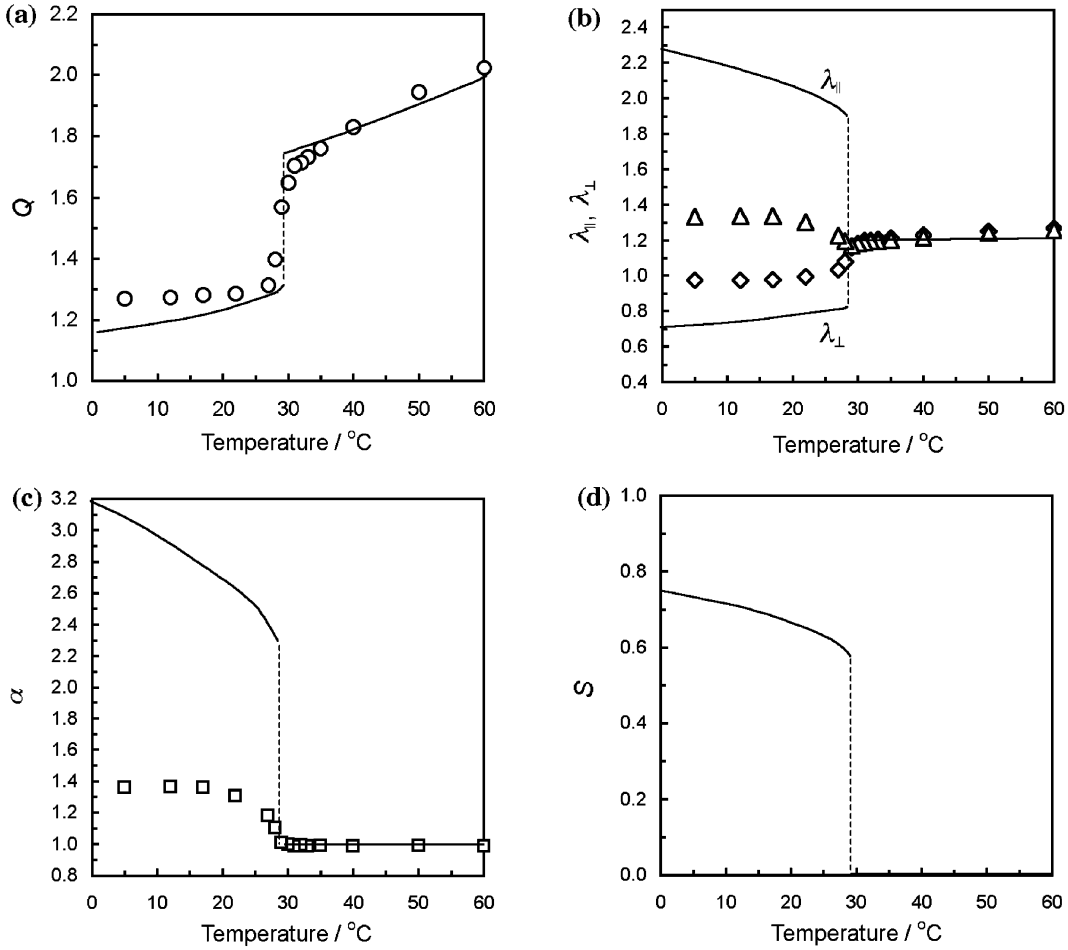


Figure 5. Comparison of the theoretical prediction with the data of the monodomain nematic network in di-*n*-butyl phthalate (DBP) for (a) equilibrium swelling degree (Q), (b) equilibrium principal ratios in the directions parallel and perpendicular to the director axis ($\lambda_{\parallel}$ and $\lambda_{\perp}$(, respectively), (c) shape anisotropy $\alpha = \lambda_{\parallel}/\lambda_{\perp}$, and (d) the theoretical order parameter S calculated simultaneously with the corresponding Q. The values of parameters used for the data-fitting are $\phi^0 = 0.5$, $S^0 = 0.5$, $n = 80$, $n_m = 2.9$, $p = 0.15$, $\chi_1/\nu = 0.417$ where χ_1 is given by $\chi = \chi_1/T$. The solid lines represent the predictions of the theory yielding a sharp N−I transition at 29 °C.

the monodomain nematic network is maintained even after repeating the N−I transition.

Our previous study[3] showed that the polydomain nematic networks in the same solvents (DBP and DAP) also undergo a volume transition at the N−I transition.[27] There are, however, the two marked differences in the swelling and volume transition behavior between the polydomain and monodomain systems. The first is that the polydomain nematic gels swell isotropically even in the nematic phase, while the monodomain nematic gels show an anisotropic swelling. This difference is simply attributed to whether the nematic director in the gels is globally oriented. The second is that the volume transition of the polydomain systems occurs discontinuously at a definite temperature whereas that of the monodomain systems takes place continuously within a narrow temperature range. The continuous volume transition of "swollen" monodomain nematic networks is qualitatively similar to a smooth change without discontinuity for both the shape and the orientational order parameter in "dry" monodomain nematic networks at the N−I transition.[2,8−14] There exist two possible reasons for the smooth transition of the dry monodomain nematic networks. A possible explanation is based on the effect of the internal stress on a first-order transition. The classical theory predicts that the discontinuity in the orientational order parameter can vanish under the stresses beyond a critical stress.[28] Meanwhile, Selinger et al.[14] showed that the applied stress yields a shift of the N−I transition temperature (T_{NI}) but no significant change in the sharpness of the transition, which disagrees with the prediction of the classical theory. They accounted for the smooth transition in terms of a finite distribution of T_{NI} resulting from the heterogeneity of orientational order formed in the cross-linking process.[14] Thus, the origin of the smooth transition still remains an open question. Our results on the volume transitions of "swollen" nematic networks may bring an important key to solve this issue: The discontinuity observed in polydomain systems is lost in monodomain systems. In contrast, in the "dry" networks, such a comparison yields no informative results because the dry polydomain systems show no definite variation in shape and volume at T_{NI}. Further studies on the volume transitions of swollen nematic networks will contribute to elucidate the origin of the smooth transition in monodomain systems.

Parts a−c of Figure 5 show the comparison of the experimental T dependence of Q, λ, and α in the DBP system with the fitted theoretical curve, respectively. Part d of the figure illustrates the theoretical values of S obtained simultaneously with the corresponding Q. The solid lines in each part of the figure depict the theoretical results. The theory successfully describes the large decrease in Q upon nematic ordering, although it predicts a discontinuous jump of Q in disagreement with the smooth volume change observed. The present theory inevitably yields a sharp transition at $T_{NI}{}^{G}$, because it treats the N−I transition as a first-order phase transition. The theory also predicts an anisotropic shape variation which takes plase simultaneously with a volume reduction upon nematic ordering. Apart from the overestimation in the degree of shape anisotropy, the theory describes the important features of the anisotropic swelling in the experiment: The length of the shrunken nematic gel in the director direction is larger than that of the swollen isotropic gel, and the shape anisotropy increases upon cooling. The trend of the theoretical prediction for α accords with the experimental data at temperatures relatively close to $T_{NI}{}^{G}$, while it does not agree with almost constant α in the low T region observed. The analogous maximum shape anisotropy at temperatures far below the N−I transition temperature was also observed in the spontaneous shape change of the acrylate-based side chain nematic network in the dry state.[12]

The excessive shape anisotropy in the theory is probably due to the overestimation of S. The theoretical values of S in the nematic phase exceed 0.5, independently of the values of fitting parameters. As seen in eq 17, α increases with increasing S. Equation 17 with $\alpha \approx 1.4$ in the experiment yields $S \approx 0.2$, fairly below the values calculated by the mean field theory. Thomsen et al.[12] reported that the maximum of S for the similar acrylate-based side chain nematic network is as large as 0.3 in the dry state. The experimental data of S in the present system will be helpful to discuss this issue strictly, but unfortunately, a direct measurement of S for the swollen network with the surrounding solvent is precluded by the experimental difficulties at present.

Conclusions

The monodomain nematic networks in isotropic solvents exhibit the smooth transition between the swollen isotropic and shrunken monodomain nematic states within a narrow temperature range. The formation of the monodomain nematic phase yields not only a significant decrease in gel volume but also an anisotropic shape variation: The length in the director direction becomes longer than that in the isotropic phase, despite a considerable volume reduction upon nematic ordering. As temperature decreases, the shape anisotropy of the nematic gels grows without appreciable volume change, and becomes almost constant at the temperatures far below $T_{NI}{}^{G}$. The volume transition accompanied by the anisotropic shape variation takes place thermoreversibly. The theory in the present study successfully describes the main features of the experimental data, although it overestimates the shape anisotropy and predicts a sharp transition in disagreement with the smooth transition observed.

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(26) The mixing of isotropic solvents and A-6OCB is not appropriate for this purpose, because a uniform nematic phase is unattainable due to the phase separation.
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