EUROPHYSICS LETTERS 1 February 1999

Europhys. Lett., **45** (3), pp. 341-347 (1999)

Elastic interactions in nematic elastomers and gels

N. Uchida and A. Onuki

Department of Physics, Kyoto University - Kyoto 606, Japan

(received 17 September 1998; accepted in final form 20 November 1998)

PACS. 64.70Md – Transitions in liquid crystals.
PACS. 61.30Cz – Theory and models of liquid crystal structure.
PACS. 61.41+e – Polymers, elastomers, and plastics.

Abstract. – We investigate elastic interactions in nematic elastomers and gels using a Ginzburg-Landau model for the isotropic-nematic transition. We propose an elastic origin of the "four-leaf clover" pattern observed in depolarised light scattering from polydomain nematic elastomers. We also investigate the director fluctuation in the nematic phase. Aligned nematic states are found to be unstable below a critical elongation.

Recently there have been a number of experimental [1-4] and theoretical [5] studies on nematic elastomers, which exhibit unique mechanical properties due to the coupling between molecular orientation and strain. Monodomain nematic states have been realised with special methods of synthesis such as two-stage crosslinking, while polydomain states with textures are mostly observed under usual conditions. It has been argued [5] that the polydomains are stabilised by the network crosslinks, which have rod-like structures and impose a random orientational field acting on the network. Clarke *et al.* [6, 7] experimentally studied the mechanical and structural properties of polydomain nematic elastomers. They observed a characteristic four-peak ("four-leaf clover") pattern in depolarised light scattering images. They also obtained a unique stress-strain relation during the strain-induced polydomain-monodomain (P-M) transition.

In this letter, to better understand these complicated effects, we set up a Ginzburg-Landau model for the isotropic-nematic transition in which the orientational order parameter Q_{ij} is coupled to the elastic field. An original model was introduced long ago by de Gennes [8], who predicted a spontaneous deformation and a jump in the stress-strain curve at the transition. Warner *et al.* [5,9] constructed an affine-deformation theory applicable even deep in the nematic phase. However, they treated homogeneous cases, and not enough attention has yet been paid to inhomogeneous cases [10-12]. We shall see that the elastic field mediates long-range interactions among the spatial fluctuations of Q_{ij}. Such elastic interactions are crucial among the composition fluctuations in phase-separating metallic alloys [13,14]. In this letter we focus on the elastic effects neglecting the disordering random field [15, 16].

Ginzburg-Landau free energy. – First we consider elastomers. The Landau-de Gennes free energy [17,18] is a functional of $Q_{ij} = S(n_i n_j - \delta_{ij}/d)$ and is assumed in the simplest form

$$F_{\rm L} = \int {\rm d}\mathbf{r} \left[\frac{A}{2} \,{\rm tr}\, \mathsf{Q}^2 + \frac{B}{3} \,{\rm tr}\, \mathsf{Q}^3 + \frac{C}{4} ({\rm tr}\, \mathsf{Q}^2)^2 + \frac{M}{2} \sum_{ijk} (\nabla_i Q_{jk})^2 \right], \tag{1}$$

where $A = a(T - T_0)$ depends on the temperature, and B, C and M are constants. The phase transition is weakly first order if B is small but non-vanishing. The elastic free energy of a non-nematic rubber under an affine deformation is written as $F_{\rm el} = \frac{1}{2} k_{\rm B} T \nu_0 V_0 \sum_i \lambda_i^2$ in the classical rubber theory [19], where V_0 and ν_0 are the volume and crosslink density before the deformation and $\lambda_1, \lambda_2, \lambda_3$ are the principal elongation ratios. More generally, if the Cartesian coordinates of material points before and after the deformation are denoted by $\mathbf{r}_0 = (x_{01}, x_{02}, x_{03})$ and $\mathbf{r} = (x_1, x_2, x_3)$, respectively, this free energy is written as $F_{\rm el} = \frac{1}{2} k_{\rm B} T \nu_0 \int {\rm d}\mathbf{r} \sum_i W_{ii}$, where $W_{ij} = \sum_k (\partial x_i / \partial x_{0k})(\partial x_j / \partial x_{0k})$ is the symmetric deformation tensor. For nematic networks crosslinked in an isotropic state, we add the lowest-order coupling between Q_{ij} and W_{ij} as

$$F_{\rm el} = \frac{1}{2} k_{\rm B} T \nu_0 \int {\rm d}\mathbf{r} \left[\sum_i W_{ii} - \sum_{ij} \alpha Q_{ij} W_{ij} \right]. \tag{2}$$

Olmsted and Milner [10] proposed a similar elastic coupling for nematic gels near the I-N transition. Warner *et al.* [5,9] assumed the form $F_{el} = \frac{1}{2} k_{\rm B} T \nu_0 V_0 \sum_{ij} \ell_0 \ell_{ij}^{-1} W_{ij}$ with $\ell_{ij}^{-1} = \ell_\parallel^{-1} n_i n_j + \ell_\perp^{-1} (\delta_{ij} - n_i n_j)$, where $\ell_\parallel$ and $\ell_\perp$ are effective step lengths of the anisotropic Gaussian chains parallel and perpendicular to $\mathbf{n}$ and ℓ_0 is the step length at the moment of isotropic crosslinking. It is rewritten in our form eq. (2) if we redefine $(\ell_0/\ell_e)\nu_0$ as ν_0 and define $\alpha = \ell_e(\ell_\perp^{-1} - \ell_\parallel^{-1})$, where $\ell_e = d/(\ell_\parallel^{-1} + (d-1)\ell_\perp^{-1})$. Thus we may use (2) even far below the I-N transition. The coupling constant α is in the range $0 < \alpha < d/(d-1)$ from $\ell_\parallel > \ell_\perp$. It is estimated to be of order 1 for main-chain elastomers and of order 0.1 for side-chain elastomers [5].

Let us first consider a network under no anisotropic external strain with small elastic displacement $\mathbf{u} = \mathbf{r} - \mathbf{r}_0$. Then to the bilinear order the elastic free energy reads [20]

$$F_{\rm el} = \int {\rm d}\mathbf{r} \left[\frac{K}{2} (\nabla \cdot \mathbf{u})^2 + \sum_{ij} \frac{\mu}{4} \left(\nabla_i u_j + \nabla_j u_i - \frac{2}{d} \delta_{ij} \nabla \cdot \mathbf{u} \right)^2 - \sum_{ij} \mu \alpha Q_{ij} (\nabla_i u_j) \right], \tag{3}$$

where $\nabla_i \equiv \partial/\partial x_i$ and $\mu = k_{\rm B} T \nu_0$ is the shear modulus. For elastomers we should take the limit $K \to \infty$ and $\nabla \cdot \mathbf{u} \to 0$, and eq. (3) reduces to the free energy introduced by de Gennes [8]. Here we keep K finite in order to discuss the case of gels later.

Elastic interaction. – The elastic field arising from the inhomogeneity in Q_{ij} is determined from the condition of mechanical equilibrium,

$$-\delta F / \delta \mathbf{u} = \Lambda \nabla (\nabla \cdot \mathbf{u}) + \mu \nabla^2 \mathbf{u} - \mu \alpha \nabla \cdot \mathsf{Q} = 0, \tag{4}$$

where $\Lambda = K + (1 - 2/d)\mu$. The Fourier components, $\mathbf{u}(\mathbf{q})$ and $\mathsf{Q}(\mathbf{q})$, are related by

$$\mathbf{u}(\mathbf{q}) = \frac{-i\alpha}{\mu q} \left[\hat{\mathbf{q}} \cdot \mathsf{Q}(\mathbf{q}) - \frac{\Lambda}{\Lambda + \mu} \hat{\mathbf{q}} (\hat{\mathbf{q}} \hat{\mathbf{q}} : \mathsf{Q}(\mathbf{q})) \right], \tag{5}$$

where $\hat{\mathbf{q}} = q^{-1}\mathbf{q}$ is the direction of the wave vector. Substituting this into $F_{\rm el}$, we obtain a bilinear elastic interaction among the fluctuations of Q_{ij}:

$$F_{\rm bi} = -\frac{1}{2} \mu \alpha^2 \int_{\mathbf{q}} \left[\left| \hat{\mathbf{q}} \cdot \mathsf{Q}(\mathbf{q}) \right|^2 - \frac{\Lambda}{\Lambda + \mu} \left| \hat{\mathbf{q}} \hat{\mathbf{q}} : \mathsf{Q}(\mathbf{q}) \right|^2 \right], \tag{6}$$

where $\int_{\mathbf{q}} = (2\pi)^{-d}\int \mathrm{d}\mathbf{q}$. This elastic interaction is simplified in the two-dimensional case where both the director and the displacement vector are confined in a plane. Such a planar director configuration is also assumed by Clarke *et al.* [6, 7] to analyse scattering from thin samples. It is convenient to introduce a new set of independent variables in the Fourier space as

$$Q_1(\mathbf{q}) = \sin(2\theta)Q_{xx}(\mathbf{q}) - \cos(2\theta)Q_{xy}(\mathbf{q}), \tag{7}$$

$$Q_2(\mathbf{q}) = \cos(2\theta)Q_{xx}(\mathbf{q}) + \sin(2\theta)Q_{xy}(\mathbf{q}), \tag{8}$$

where θ is the azimuthal angle of $\mathbf{q} = q(\cos\theta, \sin\theta)$. Then we have

$$F_{\mathrm{bi}} = -\frac{1}{2}\mu\alpha^2 \int_{\mathbf{q}} \left[|Q_1(\mathbf{q})|^2 + \frac{\mu}{\Lambda+\mu}|Q_2(\mathbf{q})|^2 \right], \tag{9}$$

Further using $|Q_{xx}(\mathbf{q})|^2 + |Q_{xy}(\mathbf{q})|^2 = |Q_1(\mathbf{q})|^2 + |Q_2(\mathbf{q})|^2$, we may calculate the fluctuation variances in the isotropic phase in the Gaussian approximation as

$$\langle |Q_1(\mathbf{q})|^2 \rangle = k_{\mathrm{B}}T \Big/ \left(2A - \mu\alpha^2 + 2Mq^2 \right), \tag{10}$$

$$\langle |Q_2(\mathbf{q})|^2 \rangle = k_{\mathrm{B}}T \Big/ \left(2A - \frac{\mu^2\alpha^2}{\Lambda+\mu} + 2Mq^2 \right). \tag{11}$$

In two dimensions Q_1 becomes unstable below the spinodal temperature $T_R = T_0 + \mu\alpha^2/2a$ at long wavelengths. The same shift of the spinodal point follows also in three dimensions and was already derived from an analysis of homogeneous strains [8]. The shift $\mu\alpha^2/2a$ of the spinodal temperature is estimated to be of the order a few degrees for main-chain elastomers and of order 10^{-2} degrees for side-chain elastomers.

Stretching. – In experiments, when an externally applied strain is increased in polydomain states, the director is gradually oriented in the stretched direction until nearly complete alignment is finally reached (P-M transition). Consider a uniaxial deformation expressed as $x_i = \lambda_i x_{0i} + u_i$ with $\lambda_2 = \cdots = \lambda_d = (1/\lambda_1)^{1/(d-1)}$, where the deviation $\mathbf{u}$ is assumed to be small. We eliminate $\mathbf{u}$ using the mechanical equilibrium condition $\delta F/\delta \mathbf{u} = 0$ to obtain two effective interactions [20]. One is linear in Q_{ij},

$$F_{\mathrm{lin}} = -\frac{1}{2}\mu\alpha \int \mathrm{d}\mathbf{r} \sum_i \lambda_i^2 Q_{ii} = -\frac{1}{2}\mu\alpha(\lambda_1^2 - \lambda_2^2) \int \mathrm{d}\mathbf{r}\; Q_{xx} + \mathrm{const}, \tag{12}$$

which favours alignment of the director in the stretched direction. The other is bilinear in Q_{ij} and is written in the Fourier space as

$$F_{\mathrm{bi}} = -\frac{1}{2}\mu\alpha^2 \int_{\mathbf{q}} \left[\sum_j \left| \sum_i \lambda_i^2 \hat{q}_i Q_{ij}(\mathbf{q}) \right|^2 - \left| \sum_{ij} \lambda_i^2 \hat{q}_i \hat{q}_j Q_{ij}(\mathbf{q}) \right|^2 \right] \Big/ \left[\sum_i \lambda_i^2 \hat{q}_i^2 \right], \tag{13}$$

which cannot be positive and reduces to eq. (6) in the isotropic case ($\lambda_1 = 1$). Here the incompressible limit ($K = \infty$) is taken for simplicity. Let us discuss the stability of a nematic state aligned in the x-axis with $S = S_0$(=const). For the director fluctuation $\delta\mathbf{n} = \mathbf{n} - \mathbf{e}_x$, where $\mathbf{e}_x$ is the unit vector in the x-axis, the elastic interaction bilinear in $\delta\mathbf{n}$ reads

$$F_{\mathrm{lin}} + F_{\mathrm{bi}} = \frac{1}{2}\mu\alpha S_0 \int_{\mathbf{q}} \sum_{ij} \left[(\lambda_1^2 - \lambda_2^2)\delta_{ij} - \alpha S_0 \varphi_{ij}(\hat{\mathbf{q}}) \right] \delta n_i(\mathbf{q})^* \delta n_j(\mathbf{q}), \tag{14}$$

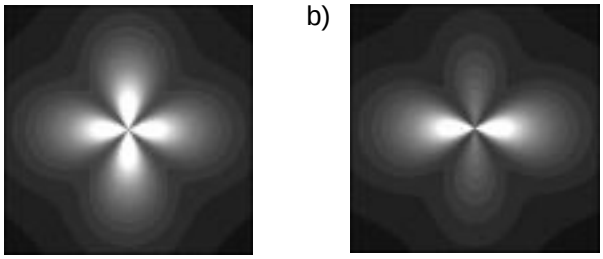

Fig. 1. – The depolarised scattering intensity $I(\mathbf{q})$ in the isotropic phase at $a(T - T_R)/\mu\alpha^2 = 0.1$. *a*) Under no external strain. *b*) Under 20% stretching in the horizontal direction.

where the summation is taken over $i, j = 2, \cdots, d$ and

$$\varphi_{ij}(\hat{\mathbf{q}}) = \left[\lambda_1^4 \hat{q}_x^2 \delta_{ij} + \left(\lambda_2^4 - (\lambda_1^2 + \lambda_2^2)^2 \hat{q}_x^2\right) \hat{q}_i \hat{q}_j\right] \Big/ \left[\lambda_2^2 + (\lambda_1^2 - \lambda_2^2)\hat{q}_x^2\right]. \tag{15}$$

We can show that the largest eigenvalue of $\varphi_{ij}(\hat{\mathbf{q}})$ takes its maximum value λ_1^2 at $\hat{\mathbf{q}} = \mathbf{e}_x$. Therefore, if $\alpha S_0 > 1$, the aligned nematic state is unstable for any stretching λ_1. On the other hand, if $\alpha S_0 < 1$, it can be stable above (but unstable below) a critical stretching λ_c given by

$$\lambda_c = 1/(1 - \alpha S_0)^{(d-1)/2d}. \tag{16}$$

The Frank free energy gives rise to a contribution proportional to q^2 in the brackets of eq. (14), which is negligible at long wavelengths (say, on micron scales). The above λ_c increases with lowering the temperature and diverges as $\alpha S_0 \to 1$. This is consistent with the observed P-M transition behaviour, where the threshold increases as a function of the quench depth [7] and is typically very large ($\lambda_1 \sim 5$) for main-chain elastomers [21]. However, on the P-M transition the effect of quenched disorder [15, 16] is also crucial, and its study will be reported in the future.

Note that the above undulation instability is obtained for isotropically crosslinked networks and should be distinguished from the stripe instability [3] for networks crosslinked in a monodomain state. In the latter case, the anisotropy of crosslinking serves as a stabilising external field for the director undulations [5, 11].

Scattering pattern. – Now we consider the depolarised light scattering intensity from a thin elastomer sample in the xy-plane. We may use the above two-dimensional results to analyse this intensity, which is proportional to $I(\mathbf{q}) \equiv \langle |Q_{xy}(\mathbf{q})|^2 \rangle$ if the incident light is polarised in the x direction and the scattered light in the y-direction [6, 7]. If the director is confined in the xy-plane, it is rewritten as

$$I(\mathbf{q}) = \cos^2(2\theta)\langle |Q_1(\mathbf{q})|^2 \rangle + \sin^2(2\theta)\langle |Q_2(\mathbf{q})|^2 \rangle. \tag{17}$$

This intensity is enhanced in the directions $\theta = n\pi/2$ (n:integer) if the fluctuations of Q_1 are larger than those of Q_2. For example, the intensity slightly above the spinodal point is calculated using eqs. (10) and (11) (fig. 1*a*)). Under stretching the intensity is more enhanced in the stretched direction (fig. 1*b*)).

The experiments [6, 7] were performed on polydomains in the nematic phase. The intensity had peaks at $\theta = n\pi/2$, which were less intense in the stretched direction than in the

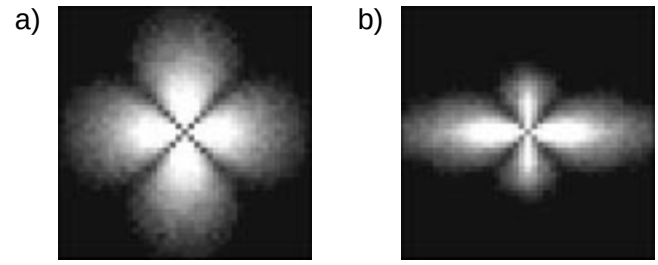

Fig. 2. – The calculated scattering intensity $I(\mathbf{q})$ in the non-linear regime of phase ordering. *a*) Under no external strain. *b*) Under 10% stretching in the horizontal direction. Statistical average over 50 runs is taken for each case.

perpendicular direction. To explain their findings, we consider phase ordering dynamics below the transition governed by the simplest dynamic equation in two dimensions,

$$\frac{\partial}{\partial t}Q_{ij} = -L_0 \frac{\delta}{\delta Q_{ij}}\left(F_{\rm L} + F_{\rm lin} + F_{\rm bi}\right). \tag{18}$$

First we consider the case without external strain. For deep quenches, $|T - T_R| \gg \mu\alpha^2/a$, no significant anisotropy in the scattering intensity is expected in the initial regime because the growth rates of Q_1 and Q_2 are almost the same. On the other hand, in the non-linear regime where $\mathrm{tr}\,\mathsf{Q}^2 \sim 1$ (far from the defect cores), the Frank free energy density and the elastic free energy density are of order M/R^2 and $\mu\alpha^2$, respectively. The R is the correlation length in the director orientation (or the average separation between defects) and grows in the coarsening process. Then there arises a crossover length given by $R_{\rm c} = (M/\mu\alpha^2)^{1/2}$. For example, for $M \sim 10^{-11}$N, $\mu \sim 10^5$J/m^3 and $\alpha \sim 10^{-1}$, we have $R_{\rm c} \sim 10^{-1}\mu$m. In the late stage where $R \gtrsim R_{\rm c}$, the elastic free energy becomes dominant and $\langle|Q_1(\mathbf{q})|^2\rangle$ should be significantly larger than $\langle|Q_2(\mathbf{q})|^2\rangle$. This condition should have been realised in the experiments [6, 7], where textures were frozen at $R \gtrsim 1\mu$m due to disorder.

To test the above scenario we numerically solved eq. (18) on a 256×256 lattice with the periodic boundary condition. The parameters used are $A = -0.875, C = 0.5, M = 0.5, \mu = 1.0$ and $\alpha = 0.5$ with the lattice spacing equal to 1. The intensity $I(\mathbf{q})$ in the non-linear regime is shown in fig. 2*a*). We can see the expected angular dependence which becomes apparent for $R \gtrsim R_{\rm c}$. However, the calculated intensity monotonically increases as $q \to 0$ in the x and y directions, whereas the experimental intensity has a minimum at small q. Furthermore, the intensity is most enhanced in the stretched direction in our simulation (fig. 2*b*)) but in the perpendicular direction in the experiments.

Gels. – For nematic gels swollen by isotropic solvent [22] or short polymer chains [10] the same model with a finite bulk modulus may be used. The nature of the lowest-order coupling is unchanged. However, we should note that there arises an important coupling in the next higher order. Gels are compressible ($\nabla \cdot \mathbf{u} \neq 0$) and $K = \phi(\partial\Pi/\partial\phi)_T$ has the meaning of the osmotic bulk modulus, Π being the osmotic pressure. The network (polymer) volume fraction $\phi = \bar{\phi} + \delta\phi$ is then related to the elastic field by $\delta\phi/\bar{\phi} = -\nabla \cdot \mathbf{u}$ where $\bar{\phi}$ is the average and $\delta\phi$ is the deviation. In gels we should take into account the ϕ-dependence of the coefficient A in eq. (1). For weakly first-order phase transitions (where B is small), we may set $A(\phi) = A(\bar{\phi}) + \beta\delta\phi/\bar{\phi}$ with $\beta = \phi(\partial A/\partial\phi)$. Then we have an additional coupling of the form([1])

$$F' = -\beta \int \mathrm{d}\mathbf{r}\ (\mathrm{tr}\,\mathsf{Q}^2)(\nabla \cdot \mathbf{u}). \tag{19}$$

([1]) F' is typically N times larger than the same order terms derived from the elastic energy in ref. [5], where N is the average segment number between crosslinks.

Due to this coupling, networks in nematic-isotropic phase coexistence have different swelling ratios or solvent densities. Elimination of $\mathbf{u}$ from $F_{\rm el}$ and F' gives rise to two additional elastic interactions. One is quartic and only serves to shift the coefficient C in eq. (1) as $C \to C - 2\beta^2/(\Lambda+\mu)$, and the other is a cubic interaction given by

$$F_{\rm cub} = -\frac{\mu\alpha\beta}{\Lambda+\mu}\int {\rm d}\mathbf{r}\ ({\rm tr}\,\mathsf{Q}^2)\sum_{ij}\frac{1}{\nabla^2}\nabla_i\nabla_j Q_{ij}, \tag{20}$$

where $1/\nabla^2$ is the inverse operator of ∇^2 and can be expressed in terms of the Green function. At present it is not clear how this term affects the isotropic-nematic transition.

Concluding discussion. – We have analysed a Ginzburg-Landau model for nematic networks. For elastomers we have investigated the elastic effects on the fluctuations taking into account the lowest-order coupling between the order parameter and the strain. For gels there arises a cubic interaction given by eq. (10) because the transition temperature depends on the solvent density. We have found an instability of aligned nematic states below a critical elongation. We also propose the elastic origin of the "four-leaf clover" pattern observed in the scattering experiments. However, we cannot explain observations such as the intensity minimum at small wave numbers and the anisotropy in the scattering pattern under stretching. To reproduce them we need to extend our model and its analysis. First, it should be clarified whether or not the samples in the experiments can be treated as a two-dimensional system. Second, because large deformations are induced deep in the nematic phase, we need to retain higher-order terms in the order parameter and the strain in the free energy. This may be carried out using the affine deformation theory by Warner *et al.* [5, 9]. Third, we need to analyse the effect of orientational disorder due to the rod-like crosslinks. Fourth, there should be heterogeneities in the crosslink density. Under stretching they should give rise to random long-ranged strain field $\mathbf{u}_{\rm R}(\mathbf{r})$ in mechanical equilibrium [20, 23]. In gels the resultant density variation ($\propto \nabla\cdot\mathbf{u}_{\rm R}$) is known to produce abnormal scattering patterns enhanced in the stretched direction. These disorder effects on the polydomain structure and the mechanical properties are currently under investigation.

REFERENCES

[1] Zentel R., *Liq. Cryst.*, **1** (1986) 586.

[2] Schätzle J., Kaufhold W. and Finkelmann H., *Macromol. Chem.*, **190** (1989) 3269; Küpfer J. and Finkelmann H., *Macromol. Chem. Rapid Commun.*, **12** (1991) 717.

[3] Kundler I. and Finkelmann H., *Macromol. Chem. Rapid Commun.*, **16** (1995) 679.

[4] Legge C. H., Davis F. J. and Mitchell G. R., *J. Phys. II*, **1** (1991) 1253; Mitchell G. R., Davis F. J. and Guo W., *Phys. Rev. Lett.*, **71** (1993) 2947.

[5] Warner M. and Terentjev E. M., *Prog. Polym. Sci.*, **21** (1996) 853, and references quoted therein.

[6] Clarke S. M., Nishikawa E., Finkelmann H. and Terentjev E. M., *Macromol. Chem. Phys.*, **198** (1997) 3485.

[7] Clarke S. M., Terentjev E. M., Kundler I. and Finkelmann H., *Macromolecules*, **31** (1998) 4862.

[8] de Gennes P. G., *C. R. Acad. Sci.*, **B281** (1975) 101.

[9] Warner M., Gelling K. P. and Vilgis T. A., *J. Chem. Phys.*, **88** (1988) 4008.

[10] Olmsted P. D. and Milner S. T., *Macromolecules*, **27** (1994) 6648.

[11] Olmsted P. D., *J. Phys. II*, **4** (1994) 2215.

[12] Terentjev E. M., Warner M. and Verwey G. C., *J. Phys. II*, **6** (1996) 1049.

[13] Cahn C. W., *Acta Metall.*, **9** (1961) 795.

[14] ONUKI A., *J. Phys. Soc. Jpn.*, **58** (1989) 3065; *J. Phys. Soc. Jpn.*, **58** (1989) 3069.
[15] FRIDRIKH S. V. and TERENTJEV E. M., *Phys. Rev. Lett.*, **79** (1997) 4661.
[16] YU Y.-K., TAYLOR P. L. and TERENTJEV E. M., *Phys. Rev. Lett.*, **81** (1998) 128.
[17] DE GENNES P. G. and PROST J., *The Physics of Liquid Crystals*, second edition (Oxford, 1993).
[18] DE GENNES P. G., *Mol. Cryst. Liq. Cryst.*, **12** (1971) 193.
[19] FLORY P. J., *Principles of Polymer Chemistry* (Cornell University, Ithaca, New York) 1953.
[20] ONUKI A., *J. Phys. Soc. Jpn.*, **57** (1988) 699; *Phys. Rev. A*, **39** (1989) 5932; *Adv. Polym. Sci.*, **109**, *Responsible Gels: Volume Transitions I* edited by K. DUSEK (Springer) 1993, p. 63.
[21] BERGMANN G. H. F., FINKELMANN H., PERCEC V. and ZHAO M., *Macromol. Rapid. Commun.*, **18** (1997) 353.
[22] WARNER M. and WANG X. J., *Macromolecules*, **25** (1992) 445.
[23] MENDES E., LINDNER P., BUZIER M., BOUE F. and BASTIDE J., *Phys. Rev. Lett.*, **66** (1991) 1595.