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Swelling Equilibria of Networks in Nematogenic Solvents

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A theory of swelling equilibria of isotropic networks in nematic solvents is given. It is based on the Flory lattice model adapted for mixtures of flexible polymers with thermotropic nematic liquid crystals. The degree of swelling exhibits an anomaly at the isotropic to nematic transition temperature of the solvent. Below this temperature the network shrinks continuously to a size hardly exceeding the dimensions of the dry state.

Keywords: Lattice model; networks swelling equilibria; rubber elasticity

INTRODUCTION

The swelling of networks by isotropic solvents is one of the classical subjects of polymer physics.[1,2] The degree of swelling observed as function of solvent power, temperature and degree of cross-linking can be understood[3–6] in terms of the recent theory of rubber elasticity introduced by Flory.[3,4] The goal of the present work is to extend this treatment to include swelling equilibria in nematogenic solvents, i.e., in solvents exhibiting a transition from the isotropic to the nematic state at a certain temperature.

The first theoretical treatment of this problem has been given by Brochard[7] using the Landau-deGennes expansion for the description of the nematic state. The elastic contribution of the network is described in terms of the Flory-Rehner theory.[1,8] The present investigation is a continuation of studies on phase equilibria in solutions of flexible polymers in nematic solvents.[9,10] In general, coiled polymers and thermotropic nematic liquid crystals have a strong tendency for demixing, i.e., the ordered phase contains only small amounts of the polymeric species. The exclusion of coils from the nematic phase becomes more pronounced with increasing length of the polymer. Since a network corresponds to a polymer chain with infinite molecular weight,[8] this incompatibility is expected to play a major role when considering swelling equilibria of such networks with nematic solvents.

An explanation of the incompatibility of rods and coils in terms of a lattice model[11] has been given first by Flory.[12] The extension of this idea originally developed for lyotropic systems (cf. Reference 12) to thermotropic systems[9] gives a

qualitatively correct description of the resulting phase diagrams.[13] These considerations can be used also for a description of swelling equilibria in nematic solvents going along the following lines: As the theory of Brochard[7] the present treatment is a mean-field approach. The starting point is given by the hypothesis that the elastic and the mixing free energies are separable. Recently, this assumption has been subject of much controversy.[6,14-17] Swelling experiments on polystyrene networks by Erman and Baysal[6] suggest this assumption to be justified for isotropic systems in general (cf. also the review of Orwoll[14]). On the other hand, this hypothesis has been challenged on the base of experimental data by Neuburger and Eichinger.[15] McKenna, Flynn and Chen[16,17] have stated that the interaction parameter χ used in the Flory-Rehner theory depends on the cross-link density. But according to these authors the elasticity of the swollen network is unaltered by the presence of the solvent other than by chain deformation. An interesting extension of the Flory-Rehner theory has been proposed by Deloche and Samulski[18] by introducing segment-segment and segment-solvent orientational correlations. The present treatment adopts the original Flory-Rehner hypothesis as a starting point. It will become evident, however, that possible improvements can be easily incorporated into theory. Hence, swelling equilibria using nematic solvent may be used as a further check of the Flory-Rehner hypothesis.

At the present level of approximation the coupling of the order of the solvent molecules to the orientation of the chains in the network[7] is disregarded. A recent investigation of the radius of gyration of polystyrene dissolved in the nematic as well as in the isotropic phase of the nematic liquid crystal PAA (*p*-azoxy anisole) has demonstrated that the distortion of chain conformation by the nematic order is very small.[19] Thus the coupling of the orientation of the solvent molecules and the orientation of the chains induced by stretching of the network is disregarded at the present level of approximation.

Starting from these premises the mixing free energy of the network and the nematogen is evaluated using the free energy for mixtures of coils with thermotropic nematogens devised recently.[9] The elastic part of the free energy is introduced in terms of the Flory-Erman model[3-5] taking into account the restriction of junction fluctuations by entanglements. Starting from these premises the present treatment allows the calculation of the swelling equilibria without resort to additional parameters.

THEORY

Assuming the contribution of the networks to the free energy to be separable from the intermolecular free energy, the Helmholtz free energy of the system may be expressed by[1,8]

$$\Delta F = \Delta F_M + \Delta F_{el} \tag{1}$$

The first term designated by the subscript M describes the changes of the free energy due to compositional changes as well as to alterations pertaining to the

difference in free volume at fixed chemical content. The second term relates to the elastic contribution of the network. Accordingly, we have

$$\Delta\tilde{\mu}_r \equiv (\mu_r - \mu_r^o)/RT = \Delta\tilde{\mu}_{r,M} + (RT)^{-1}(\partial\Delta F_{el}/\partial n_r) \tag{2}$$

for the reduced chemical potential of the nematogenic diluent denoted by the subscript r, with n_r being the number of moles of the diluent.

In order to evaluate the first term, the neat nematic liquid as well as the mixture of a nematogen with the network may be described in terms of the Flory lattice model as outlined previously.[9] Hence the order present in the solvent is described by the disorder index y[11]

$$y = (4/\pi)x_r \sin\psi \tag{3}$$

where x_r is the axial ratio of the rod-like solvent molecule and ψ denotes the angle of inclination towards the domain axis. The orientation-dependent energy ε_ψ of one segment of the rod-like particle follows as[9,11]

$$-\varepsilon_\psi = (k_B T^*/\tilde{V})v_r s\left(1 - \frac{3}{2}\sin^2\psi\right) \tag{4}$$

with T^* being the characteristic temperature and $\tilde{V}$ the reduced volume; the quantity s is the familiar order parameter. The dilution of the anisotropic forces by the network is taken into account by the factor v_r, the volume fraction of the thermotropic species. The orientational distribution of the nematogenic molecules, i.e., the ratio of the number n_{ry} of molecules having the disorder index y to their total number n_r may be expressed by[9,11]

$$\frac{n_{ry}}{n_r} = (\sin\psi/f_1)\exp\left(-\frac{4}{\pi}ax_r\sin\psi - \frac{3}{2}\frac{v_r x_r s}{\tilde{V}\Theta}\sin^2\psi\right) \tag{5}$$

with[11,9]

$$a = -\ln\left[1 - \frac{v_r}{\tilde{V}_r}\left(1 - \frac{\bar{y}}{x_r}\right)\right] \tag{6}$$

where $\tilde{V}_r$ is the reduced volume of the nematogenic diluent, and $\bar{y}$ denotes the disorder index at equilibrium. The quantity f_1 is the first member of the integrals[11,9]

$$f_p = \int_0^{\pi/2} \sin^{p-1}\psi\left(\frac{n_{ry}}{n_r}\right)d\psi \tag{7}$$

The reduced temperature Θ is defined by $= T/T^*$. Since the segments of the

network are assumed not to take part in the ordering process, the total change of energy of the system due to the ordering transition follows as[9]

$$E_{\text{orient}} = -\frac{1}{2} n_r x_r \frac{v_r s^2}{\tilde{V}\Theta} \tag{8}$$

The change of energy caused by isotropic interaction between the solvent and the segments of the network is formulated in terms of the interaction parameter χ or a characteristic temperature T_i^* of isotropic interaction[9]

$$\Delta H_M = n_r x_r v_c \chi = n_r x_r v_c \frac{T_i^*}{T} \tag{9}$$

where v_c is the volume fraction of the polymeric species. Equation (9) corresponds to an interaction parameter independent of polymer concentration.[8] The present treatment, however, is easily extended to take into account the dependence of χ on v_c.

Pursuant the derivation of the free energy of mixing ΔF_M we may go along the lines of the classical theory of Flory and Rehner.[1,8] Thus for the mixture of rods with a network under consideration here the expression for the mixing partition function given in Reference 9 may be taken. It has to be borne in mind that the number of polymer molecules is to be equated to zero owing to the absence of individual polymer molecules in the network. Accordingly, the chemical potential for the nematogen as derived in Reference 9 (Equation (4)) may be taken if the number of segments of the polymeric species is going to infinity. With $\tilde{V}_c$ being the reduced volume of the network $\Delta\mu'_{r,M}$ in the ordered phase follows as:

$$\Delta\mu'_{r,M}/RT = \ln \frac{(1 - v'_c)}{x_r \tilde{V}_r} + (1 - v'_c)(\bar{y} - 1) + v'^2_c x_r$$

$$+ x_r \left(\frac{\tilde{V}_r}{\tilde{V}'} - 1 \right) + x_r(\tilde{V}_r - 1) \left[a + \ln \left(1 - \frac{1}{\tilde{V}'} \right) \right] - \ln f_1$$

$$- \frac{V_r x_r s}{\tilde{V}'\Theta} \left[1 - s(1 - v'_c) \left(1 - \frac{1}{2} \frac{\tilde{V}'}{\tilde{V}_r} \right) \right] + \chi x_r v'^2_c \tag{10}$$

where the primes mark quantities referring to nematic state. The corresponding quantity for the isotropic phase may be derived by equating of y to x and of s to zero is

$$\Delta\mu_{r,M}/RT = \ln \frac{(1 - v_c)}{x_r \tilde{V}_r} + x_r - 1 + v_c + x_r \left(\frac{\tilde{V}_r}{\tilde{V}} - 1 \right)$$

$$+ x_r(\tilde{V}_r - 1) \ln (1 - \tilde{V}^{-1}) + \chi x_r v_c^2 \tag{11}$$

Note that in both cases the pure isotropic solvent at $\tilde{V} = 1$ has been taken as the

state of reference. Therefore $\Delta\mu_{r,M}$ does not reduce to zero at $v_c = 0$, but contains a residual term because of the entropy contribution by the free volume. Owing to the small difference of the densities of the nematic and the isotropic state, $\tilde{V}_r'$ has been set equal to $\tilde{V}_r$. However, since $\tilde{V}$ depends on composition, $\tilde{V}'$ may differ from $\tilde{V}$.

Following the analysis of Flory,[4] and of Erman and Flory[5] the network is characterized by its cycle rank ξ expressing the number of independent circuits. For the perfect network we have[3]

$$\xi = \mu_j \left(\frac{1}{2}\phi - 1\right) = \nu\left(1 - \frac{2}{\phi}\right) \tag{11}$$

where μ_j is the number of junctions, ϕ the functionality, and ν the number of linear chains. According to the molecular theory of rubber elasticity the elastic free energy for isotropic dilatation by a linear factor λ is given by[4,5]

$$\Delta F_{el} = \frac{3}{2} kT[\xi(\lambda^2 - 1) + \mu_j(1 + \lambda^2/\kappa)B - \mu_j \ln [1 + B(1 + \lambda^2 B/\kappa)] \tag{12}$$

and

$$B = (\lambda^2 - 1)/(1 - \lambda^2/\kappa)^2 \tag{13}$$

and λ relates to v_c by

$$\lambda = (v_c^0/v_c)^{1/3} \tag{14}$$

with v_c^0 being the volume fraction of the polymer in the state of reference.

The quantity κ measures the constraints on fluctuations of junctions due to the surrounding chains in which they are embedded.[3] If κ is vanishing, Equation (12) describes the phantom network. At the opposite extreme, fluctuations of the junctions may be considered to be suppressed totally if κ is going to infinity (affine limit). The elastic contribution of the network to the chemical potential of the diluent under conditions of isotropic swelling may be derived from (12) by[4,5]

$$\Delta\tilde{\mu}_{r,el} = (RT)^{-1} (\partial \Delta F_{el}/\partial\lambda)(\partial\lambda/\partial n_r) \tag{15}$$

Thus[4]

$$\Delta\tilde{\mu}_{r,el} = (V_r/V_0 N_A \lambda)[\xi + \mu_j K(\lambda)] \tag{16}$$

where V_r is the molar volume of the solvent and V_0 is the volume of the relaxed

network, i.e., the volume of the polymer when the cross-linkages are induced. The quantity $K(\lambda)$ results to[5]

$$K(\lambda) = B[\dot{B}(1 + B)^{-1} + (\lambda/\kappa)^2(B + \lambda^2\dot{B})(1 + \lambda^2 B/\kappa)^{-1}] \tag{17}$$

with

$$\dot{B} = \partial B/\partial\lambda^2 = B[(\lambda^2 - 1)^{-1} - 2(\lambda^2 + \kappa)^{-1}] \tag{18}$$

For a perfect tetrafunctional network we have accordingly

$$\Delta\tilde{\mu}_{r,\mathrm{el}} = (v_c^o V_r/V_o N_A\ \lambda)(\nu/2)[1 + K(\lambda)] \tag{19}$$

If the front factor is expressed in terms of the number x_c of segments per linear chain, $\bar{v}$ denotes the specific volume of the polymer and M_c the average molecular weight per crosslinked unit,

$$x_c = \frac{M_c\bar{v}}{V_r} \cdot x_r \tag{20}$$

we arrive at

$$\Delta\tilde{\mu}_{r,\mathrm{el}} = (v_c^o x_r/2x_c)\lambda^{-1}\,[1 + K(\lambda)] \tag{21}$$

The degree of swelling in the isotropic solvent may be calculated by numerical solution of the corresponding equilibrium conditions

$$\Delta\mu_{r,M}(v_c \neq 0) + \Delta\mu_{r,\mathrm{el}} = \Delta\mu_{r,M}(v_c = 0) \tag{22}$$

If the solvent within the network is isotropic but nematic in the neat liquid we have

$$\Delta\mu_{r,M}(v_c \neq 0) + \Delta\mu_{r,\mathrm{el}} = \Delta\mu'_{r,M}(v_c = 0) \tag{23}$$

For the nematic-isotropic equilibrium in the neat solvent outside of the network the corresponding condition is given by

$$\Delta\mu_{r,M}(v_c = 0) = \Delta\mu'_{r,M}(v_c = 0) \tag{24}$$

The degree of swelling below the nematic-isotropic transition temperature may be calculated by numerical solution of (23) and (24) in the usual manner.[9]

RESULTS AND DISCUSSION

As already discussed in the introduction the nematic phase of a thermotropic liquid crystal expels a coiled component with great effectivity. In a biphasic equilibrium

the nematic phase therefore contains only minute amounts of the latter species which is mainly confined to the isotropic phase. This strong demixing tendency of rods and coils upon formation of an ordered phase first discussed by Flory[12] becomes more pronounced with increasing chain length of the polymer. The swelling equilibrium discussed herein corresponds to a system of a thermotropic nematogen and a coil of infinite length (see theoretical section). It is thus evident that the nematic phase cannot form inside the network consisting of flexible coils, i.e., the transition temperature from the isotropic to the nematic state will be strongly depressed inside the rubber. Therefore only equilibria where the solvent remains isotropic in the network are considered here.

Figure (1a) and (1b) display the degree of swelling $q = \lambda^3$ (cf. Equation (14)) as function of temperature for a network characterized by $x_c = 100$. The equation-of-state parameters and the characteristic data of the nematogenic solvent (cf. Figure (1a, b)) have been chosen to fit to polystyrene networks immersed in the nematic liquid crystal EBBA (*p*-ethoxybenzylidene-*p*-*n*-butylaniline). All data have been taken from Reference 9 and 10. The value of $\kappa = 10$ used throughout the model calculations is typical for polystyrene networks and has been determined by swelling experiments in isotropic solvents.[6] In Figure (1a) the characteristic temperature of isotropic interaction T_i^* (cf. Equation (9)) of 30 K corresponds to a better solvent quality than in Figure (1b) where T_i^* was chosen to 50 K.

As is obvious from Figure (1a, b) there is a strong anomaly of the swelling curve

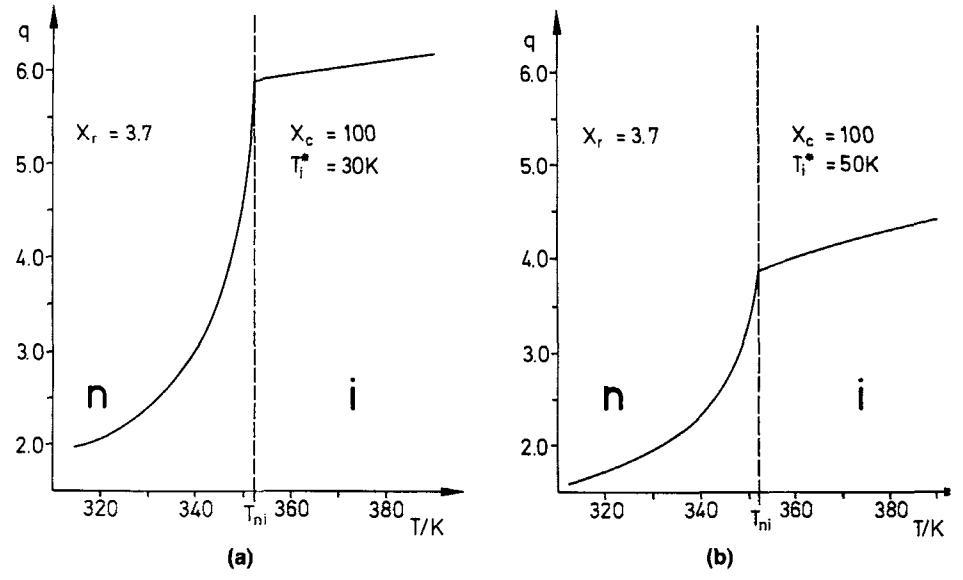

FIGURE (1a, b) Degree of swelling $q = \lambda^3 = v_c^{-1}$ as function of temperature for an isotropic network immersed in a thermotropic nematic liquid crystal. The characteristic data of the network correspond to typical values for polystyrene (κ ca. 10, cf. Reference 6); equation-of-state parameters for linear polystyrene chains, $\alpha_c = 5.77 \cdot 10^{-4}\ K^{-1}$ cf. Reference 10, α_c: thermal expansion coefficient of polystyrene). The data referring to the nematogen correspond to EBBA, (*p*-ethoxybenzylidene-*p*-*n*-butylaniline; $T^* = 351.2$ K, $T_{ni} = 352.3$ K, $\alpha_r = 8.22 \cdot 10^{-4}\ K^{-1}$, α_r: thermal expansion coefficient, $x_r = 3.7$ see Reference 10). The characteristic temperature of isotropic interaction T_i^* indicated in the graphs refers to the solvent power of the liquid crystal with regard to polystyrene chains.

at the isotropic-to-nematic transition of the solvents. The gel expels the solvent in a continuous fashion below T_{ni}. At T_{ni} the degree of swelling q extrapolated from values above and below the transition temperature coincides. This is evident from the combination of the equilibrium conditions (23) and (24) being valid together only at T_{ni}. Hence

$$\Delta\mu_{r,M}(v_c \neq 0,\ T = T_{ni}) + \Delta\mu_{r,el} = \Delta\mu_{r,M}(v_c = 0,\ T = T_{ni})$$

which is identical to the equilibrium condition (22) valid above T_{ni}. In consequence the swelling curve for $T \leq T_{ni}$ starts at a value of q extrapolated from isotropic phase to $T = T_{ni}$.

Far below T_{ni} the network has shrunk to a size hardly exceeding the dimensions in the dry state. Similar conclusions have been drawn by Brochard.[7] Thus 20 degrees below T_{ni} the uptake of the nematic swelling agent by the network is predicted to be very small. This again demonstrates the nematic ordering of the solvent inside the network will never occur, even at exceedingly low temperatures. It is evident from the fact that the volume fraction of the chains of the network disturbing nematic order is increasing rapidly with decreasing temperature. On the other hand, already small volume fractions of chains depress the isotropic to nematic transition temperature considerably. Hence, no ordering transition inside the network will occur. In consequence, the possible coupling between the flexible chains and the nematic order in the solvent need not to be included in this treatment.

However, a totally different situation arises in liquid crystalline networks.[20-22] Here nematic order is possible below a certain transition temperature. Hence the ordering of the solvent molecules below T_{ni} may couple to the orientation of the segments of the network. This could lead to nematic order within the network even in the swollen state. In this case the strong incompatibility of nematic phases and isotropic coils would no longer be present. The obvious consequence of this already pointed out by Brochard[7] is an uptake of the solvent by the network.

To the author's knowledge the only swelling experiments of isotropic networks in nematic solvents have been performed by Gebhard and Rehage[23] using trans-1,5-polypentenamer rubber and MBBA (*p*-methoxy-benzylidene-*p*-*n*-butylaniline) as the swelling agent. From the high degrees of swelling of the networks in a number of good solvents as opposed to the small values of q (1.5–2) reported[23] for the isotropic phase of liquid crystal one may infer a rather poor solvent quality of MBBA for the polymer under consideration. Thus results obtained from this system may be compared in first approximation to the model calculation displayed in Figure (1b). In accordance with the deduction derived herein Gebhard states[24] that the resulting swelling curves exhibit an anomaly at T_{ni}.

A comprehensive comparison of theory and experiment first requires the exact characterization of the network going along the lines devised by Erman and Baysal.[6] Then swelling equilibria in the isotropic phase of a suitable nematogen then furnish the interaction parameter $\chi(v_c, T)$. This in turn allows the calculation of the degree of swelling below T_{ni} as described herein provided the equation-of-state data of the nematogen are known with sufficient accuracy. A sensitive test of these parameters is provided by monitoring the phase equilibria of the nematogen with the

respective linear chains of which the network is built up. Therefore swelling experiments as outlined in this paper would be highly useful to test the validity of Equation (1) by a different type of experiment than used for this purpose up to now. At present an experimental study using polybutadiene networks swollen in nematic solvents is under way.[25]

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