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Swelling of Isotropic Networks in Nematic Solvents

H. Orendi and M. Ballauff*

Max-Planck-Institut für Polymerforschung, Postfach 3148, 6500 Mainz, Germany

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ABSTRACT: An investigation of swelling equilibria of isotropic poly(butadiene) networks in the two thermotropic nematic solvents PAA (*p*-azoxyanisole) and EBBA (*N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline) above and below the nematic-to-isotropic transition temperature is presented. The degree of swelling q as measured by the ratio of the volume of the swollen network to the volume of the dry network exhibits a strong anomaly at the transition temperature. Below the transition the network expels the solvent in a continuous fashion. All experimental data can be described quantitatively by a theory based on the Flory lattice model of nematic liquids together with the Flory–Erman theory of rubber elasticity.

Introduction

Compatible blends of rigid-rod polymers and flexible coils present an interesting type of polymer mixtures. Depending on composition, such a blend may form either an isotropic or a nematic phase. Flory[1] first recognized with the aid of a lattice model that the formation of an ordered phase is followed by a pronounced incompatibility even in athermal mixtures. Thus the nematic phase strongly excludes the coiled species solely for entropic reasons. The experimental phase diagrams[2] are in very good agreement with the theoretical result calculated by Flory's lattice model. This "entropic incompatibility" occurs not only in lyotropic mixtures of a coiled and a rodlike polymer in a common solvent but also in mixtures of thermotropic liquid crystals with flexible polymers (see the review of the experimental data in ref 3). The Flory lattice model can be easily extended to include thermotropic systems,[4] and the results again match the experimental data nearly quantitatively.[4–6] These findings unambiguously demonstrate that Flory's theory[1] is a useful tool for the description of polymer mixtures capable of forming nematic phases.

Prompted by this success of theory, Ballauff extended the lattice model to swelling equilibria of networks composed of flexible polymers in nematic liquid crystals.[7] Here the liquid crystal will act like an isotropic liquid above the nematic-to-isotropic transition temperature T_{ni}. Hence, depending on solvent power, the network will take up the nematogen to a greater or lesser extent. Exactly at T_{ni}, however, the neat liquid outside the network will become nematic but there will be no ordered phase inside the network. This is obvious from the strong depression of the transition temperature in the presence of a coiled polymer.[4] As a consequence, the uptake of solvent below T_{ni} will be greatly diminished and the network will shrink considerably.

It has to be noted that the foregoing statement only holds true if there is no coupling of the order of the network segments to the nematic order of the solvent. A recent investigation[8] 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*-azoxyanisole) has indeed demonstrated that the distortion of chain conformation by the nematic order is very small. The reason for this finding must be obviously sought in the lack of anisotropic interaction of the polystyrene segments with the nematic solvent. A totally different situation, however, arises in liquid crystalline networks containing mesogenic segments.[9–11] Here a stable nematic phase may exist inside the network, which should be followed by a considerable uptake of solvent below T_{ni}.

The first theoretical treatment of this problem was given by Brochard[12] using the Landau–de Gennes expansion[13] for the description of the nematic state. To the authors' best knowledge the only swelling experiments of isotropic networks in nematic solvents have been performed by Gebhard[14] and Rehage but no explicit data are given in their work. In this paper we present an extended discussion of swelling equilibria of networks in the nematic solvents. The predictions of theory are compared with experimental data of swelling equilibria of poly(butadiene) networks in the nematic solvents PAA and EBBA (*N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline).

Experimental Section

Materials. PAA (*p*-azoxyanisole) and EBBA (*N*-(*p*-ethoxybenzylidene)-*p*-*n*-butylaniline) were purchased from Aldrich and purified by recrystallization from ethanol. The nematic-to-isotropic transition temperatures were determined by thermal analysis and polarizing microscopy. They are in satisfactory agreement with the respective literature values (PAA, 135.6 °C (lit.[15] 135.6 °C); EBBA, 78.8 °C (lit.[16] 79.1 °C). Polybutadiene was prepared by anionic polymerization of butadiene in benzene at room temperature. As starter, oligostyrene anions were used; the termination was done by adding methanol. The weight-average molecular weight as determined by GPC was 60 000. The content of vinyl groups was 25% as measured by ^{1}H NMR. Cross-linking was achieved by using the procedure of Aranguren and Macosko.[17] The cross-linking agent was *p*-bis(dimethylsilyl)benzene (Petrach Systems) catalyzed by *cis*-dichlorobis(diethyl sulfide)platinum(II) (Strem Chemicals). In each run approximately 1 g of polybutadiene was mixed in bulk with the cross-linker and the catalyst at room temperature. After 90 min the completeness of reaction was checked by determination of the sol fraction extracted by toluene. In all cases the soluble portion after cross-linking was found to be less than 5%.

Swelling Experiments. Network + EBBA. Since in EBBA the degree of swelling as expressed by the ratio q of the volume in the swollen state to the volume in the dry state ranges between 1.3 and 4.0, measurement could be done by determining the size of a small cube of the network under the microscope. Thus a cube of approximately 1 × 1 × 1 mm was immersed in EBBA between glass slides on a Mettler FP 82 hotstage. A small piece of wire ensured a proper distance between the two slides and the absence of mechanical forces on the network. The change of the length of a given edge of the cube could be monitored by a scale etched into the ocular of the microscope (Zeiss Photomikroskop). The degree of swelling $q = V/V_0$ follows as $q = l^3/l_0^3$.

The degree of swelling in PAA never exceeded 1.4. Thus measurements conducted on a small sample would not furnish

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* To whom all correspondence should be addressed. Present address: Polymer-Institut, Universität (TH) Karlsruhe, Kaiserstrasse 12, 7500 Karlsruhe, Germany.

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data of sufficient accuracy. Therefore a strip with the approximate size 10 × 1 × 0.5 mm was used. The strip was mounted in a specially designed cell and its position was fixed on one side by a clamp. The specimen was covered by a glass slide and the whole assembly mounted on the hotstage of the microscope. The strip immersed in the liquid crystal was guided by tracks of the cell, and the change of its length upon swelling could be monitored accurately in the microscope. In both cases the degree of swelling could be determined with an accuracy of approximately 2%. Approaching a given temperature from above and below furthermore demonstrated the reproducibility of the results. If the temperature was raised above 160 °C in PAA, however, degradation of the network became a serious problem and the experiment had to be repeated with a fresh specimen.

Theory

The theoretical treatment presented in ref 7 is based on the Flory–Rehner hypothesis;[18] i.e., the free energy of mixing is separable into a mixing part ΔF_{M} and an elastic part ΔF_{el}:

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

This assumption has recently come under attack by Neuburger and Eichinger.[19] McKenna and co-workers[20-22] presented experimental evidence for the dependence of the mixing part of ΔF, i.e., of the interaction parameter χ on cross-link density. Another modification of theory has been done by Deloche and Samulski[23] through introduction of orientational correlations between the segments. On the other hand, experiments conducted by Erman and Baysal[24] on polystyrene networks suggest the Flory–Rehner theory to work well.

In addition to these difficulties, swelling experiments provide at the same time a sensitive test for the elastic part ΔF_{el}. Here Gottlieb and Gaylord[25] have shown that only a few theoretical models account for all the experimental facts. This controversy shows that despite decades of research on swelling of networks there are still a number of unresolved questions. In this paper we adopt the Flory–Rehner hypothesis as a starting point. A comparison of the theoretical deductions with experimental results will therefore serve as a test of this assumption, too.

From eq 1 the reduced chemical potential of the nematogenic swelling agent identified by the index r follows as

$$\Delta\tilde{\mu}_{\mathrm{r}} \equiv (\mu_{\mathrm{r}} - \mu_{\mathrm{r}}^{\circ})/RT = \Delta\tilde{\mu}_{\mathrm{r,M}} + (RT)^{-1}(\partial \Delta F_{\mathrm{el}}/\partial n_{\mathrm{r}}) \tag{2}$$

To evaluate the first term $\Delta\tilde{\mu}_{\mathrm{r,M}}$, the 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.[4,7] Hence the order present in the solvent is described by the disorder index y

$$y = (4/\pi)x_{\mathrm{r}} \sin \psi \tag{3}$$

where x_{r} is the axial ratio of the rodlike solvent molecule and ψ denotes the angle of inclination toward the domain axis. Since the nematic-to-isotropic transition is strongly depressed in the presence of a coiled species, the solvent inside the network will never undergo the ordering transition (cf. ref 7 for an extended discussion of this point). For the mixing part of the chemical potential of the solvent inside the isotropic network $\Delta\tilde{\mu}_{\mathrm{r,M}}$ the following expression is obtained:[7]

$$\Delta\tilde{\mu}_{\mathrm{r,M}} = \ln(1 - \upsilon_{\mathrm{c}}) + x_{\mathrm{r}} - 1 + \upsilon_{\mathrm{c}} + x_{\mathrm{r}}(\tilde{V}_{\mathrm{r}}/\tilde{V} - 1) + x_{\mathrm{r}}(\tilde{V}_{\mathrm{r}} - 1)\ln(1 - \tilde{V}^{-1}) + \chi x_{\mathrm{r}}\upsilon_{\mathrm{c}}^{2} \tag{4}$$

where υ_{c} denotes the volume fraction of the network and $\tilde{V}$ the reduced volume of the system. The latter quantity follows from the reduced volume $\tilde{V}_{\mathrm{r}}$ of the rodlike species and the respective quantity $\tilde{V}_{\mathrm{c}}$ of the coiled species as[7]

$$1/\tilde{V} = \upsilon_{\mathrm{r}}/\tilde{V}_{\mathrm{r}} + \upsilon_{\mathrm{c}}/\tilde{V}_{\mathrm{c}} \tag{5}$$

The reduced volume of the respective pure components may be calculated in the usual manner[26] using their expansion coefficients α:

$$\tilde{V}_{\mathrm{r}}^{1/3} - 1 = \alpha T/[3(1 + \alpha T)]$$

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[4]

$$\Delta H_{\mathrm{M}} = n_{\mathrm{r}}x_{\mathrm{r}}\upsilon_{\mathrm{c}}\chi = n_{\mathrm{r}}x_{\mathrm{r}}\upsilon_{\mathrm{c}}(T^*_{\mathrm{i}}/T) \tag{6}$$

where υ_{c} is the volume fraction of the polymeric species. Equation 6 corresponds to an interaction parameter independent of polymer concentration.[18]

As outlined in the Introduction, the ordered phase can only occur in the neat nematogenic liquid outside the network. Hence $\Delta\tilde{\mu}'_{\mathrm{r,M}}$ follows from the respective expression for the chemical potential given in ref 4 by equating the volume fraction υ_{c} of the coiled species to zero. The result is

$$\Delta\tilde{\mu}'_{\mathrm{r,M}} = \bar{y} - 1 + x_{\mathrm{r}}(\tilde{V}_{\mathrm{r}} - 1)[a + \ln(1 - 1/\tilde{V}_{\mathrm{r}})] - \ln f_1 - (x_{\mathrm{r}}S/\tilde{V}_{\mathrm{r}}\Theta)[1 - (1/2)S] \tag{7}$$

Here, $\bar{y}$ denotes the equilibrium value of the disorder index y as defined by eq 3, S is the common order parameter, and a is a quantity defined by

$$a = -\ln[1 - \tilde{V}_{\mathrm{r}}^{-1}(1 - \bar{y}/x_{\mathrm{r}})] \tag{8}$$

The reduced temperature Θ is defined through $\Theta = T/T^*$, where the characteristic temperature T^* provides a measure for the strength of the anisotropic interaction forces between the rodlike solvent molecules.[27] The quantity f_1 follows as

$$f_1 = \int_0^{\pi/2} \sin\psi \exp[-(4/\pi)ax_{\mathrm{r}}\sin\psi - (3/2)(x_{\mathrm{r}}S/\tilde{V}_{\mathrm{r}}\Theta)\sin^2\psi]\,\mathrm{d}\psi \tag{9}$$

The respective expression for the isotropic solvent follows from eq 7 through equating of y to x_{r} and of S to zero.

Following the analysis of Flory and Erman,[28] one obtains for the case of a perfect tetrafunctional network

$$\Delta\tilde{\mu}_{\mathrm{r,el}} = (\upsilon_{\mathrm{c}}^{\circ}x_{\mathrm{r}}/2x_{\mathrm{c}})\lambda^{-1}[1 + K(\lambda)] \tag{10}$$

for the elastic part of the chemical potential of the solvent. Here, $\upsilon_{\mathrm{c}}^{\circ}$ denotes the volume fraction of the polymer during crosslinking, x_{c} the number of segments per linear chain, and λ the linear degree of extension:

$$\lambda = (\upsilon_{\mathrm{c}}^{\circ}/\upsilon_{\mathrm{c}})^{1/3} = q^{1/3} \tag{11}$$

The quantity $K(\lambda)$ results to[28]

$$K(\lambda) = B[\dot{B}(1 + B)^{-1} + (\lambda/\kappa)^2(B + \lambda^2\dot{B})(1 + \lambda^2B/\kappa)^{-1}] \tag{12}$$

with

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

and

$$\dot{B} = B[(\lambda^2 - 1)^{-1} - 2(\lambda^2 + \kappa)^{-1}] \tag{14}$$

The parameter κ gives a measure for the constraints of the fluctuations of the network junctions due to neighboring chains.[29] If κ tends to infinity, the network corresponds to the affine limit; values of κ going to zero describe the phantom network.

The number x_c of segments per linear chain may be calculated through

$$x_c = M_c v\, x_r / V_{M,r} \tag{15}$$

where v is the specific volume of the polymer, M_c the average molecular weight per cross-link unit, and $V_{M,r}$ the molar volume of the liquid crystalline solvent. In principle, the actual volumes of the components used in eq 15 should be replaced by the respective hard-core volumes. Trial calculations showed, however, that the alterations of x_c thus effected are within experimental uncertainty.

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

$$\Delta\tilde{\mu}_{r,M}(v_c \neq 0) + \Delta\tilde{\mu}_{r,el} = \Delta\tilde{\mu}_{r,M}(v_c = 0) \tag{16}$$

If the solvent within the network is isotropic but nematic in the neat liquid, the right-hand side of eq 16 has to be replaced by eq 7. For the nematic–isotropic equilibrium in the neat solvent outside the network the chemical potential of the solvent in the ordered phase (eq 7) has to be equated to the corresponding expression for the isotropic phase and solved numerically.

Results and Discussion

As outlined in the foregoing section the present approach utilizes the Flory–Erman[29,28] theory to describe the elastic part of the free energy. Hence the constraints to the network junctions exerted through the neighboring chains are modeled by a single parameter κ where the affine limit corresponds to $\kappa \rightarrow \infty$ and the phantom limit to $\kappa = 0$. This parameter may be calculated from the characteristic data of the network and an empirical constant following the analysis of Flory and Erman.[28] Adopting this procedure, κ is expected to be of the order of 10. A value of similar magnitude has been found by Erman and Baysal[24] experimentally for swelling experiments on polystyrene networks in isotropic solvents.

Other parameters influencing the degree of swelling q as a function of temperature are the characteristic temperature of isotropic interaction T^*_i between network and solvent (cf. eq 6) and the number x_c of segments per linear chain of the network. The latter quantity may be calculated from the amount of cross-linker in the system; T^*_i is treated as an adjustable constant in this context.[4,7] Data obtained on mixtures of free poly(butadiene) chains in the respective liquid crystals would furnish independent data for this parameter, too.

Additional parameters necessary for the comparison of theory and experiment are the axial ratio of the liquid crystal used for the swelling experiment[4] (PAA, 3.6;[30] EBBA, 3.7[31]) and the density and the thermal expansion coefficients of the polymer ($\alpha = 7.5 \times 10^{-4}$ K^{-1};[32] density at 25 °C, 0.96 g/cm^3 [32]) and the liquid crystals (PAA, $\alpha = 8.36 \times 10^{-4}$ K^{-1};[33] EBBA, $\alpha = 8.22 \times 10^{-4}$ K^{-1} [34]). The latter data provide the reduced volume of the system.[26] For the network data of the free chains have been taken since the alterations of pVT data due to cross-linking can be disregarded at the present level of approximation. The characteristic temperature T^* of anisotropic interaction can be evaluated from the nematic–isotropic transition temperature, the axial ratio, and the free volume of the liquid crystal at the transition point[4] (PAA, $T^* = 444.9$ K; EBBA, $T^* = 351.2$ K (cf. refs 27 and 31)).

To assess the influence of the various parameters on the degree of swelling q as a function of temperature, we first present results of model calculations. Figure 1 displays $q(T)$ calculated for a network with $x_c = 300$ in PAA. Here, T^*_i has been equated to zero and in consequence there is no dependence of q on temperature above $T = T_{ni}$.

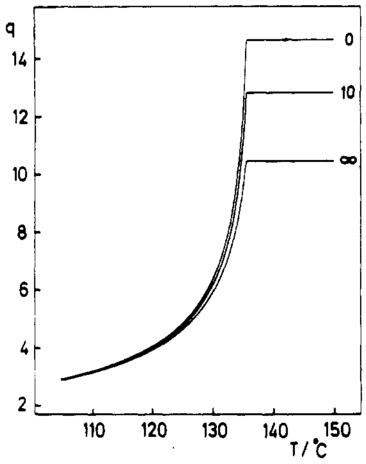

Figure 1. Degree of swelling $q(T) = V/V_0$ as a function of temperature. The calculation presented has been done for poly(butadiene) networks ($x_c = 300$; cf. eq 15) immersed in the nematic liquid crystal PAA (for the characteristic data of PAA, see text). Parameter of the different curves is κ, measuring the constraints of the network junctions exerted through neighboring chains;[29] $\kappa = 0$ corresponds to the limit of the phantom network, $\kappa = \infty$ to the affine limit.

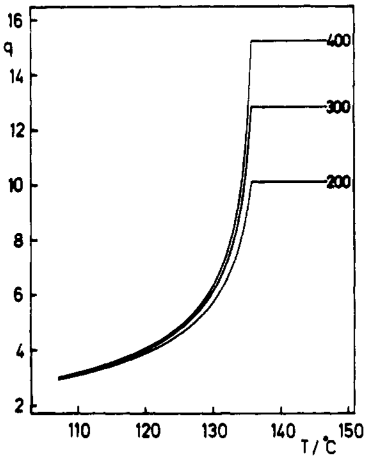

Figure 2. Degree of swelling $q(T) = V/V_0$ as a function of temperature. The calculation presented has been done for poly(butadiene) networks differing in the degree of cross-linking immersed in the nematic liquid crystal PAA (for the characteristic data of PAA, see text). Parameter of the different curves is x_c, the number of segments per linear chain.

There is a pronounced shrinking of the network below the transition temperature. The parameter κ clearly governs the uptake of solvent in the isotropic phase. Thus q for phantom networks exceeds the value obtained for the affine limit, of course. In the nematic regime, however, κ is of minor importance due to strong shrinking. Hence in this context it is adjusted to 10; for a more detailed analysis κ must be determined from independent sources.[28]

The degree of swelling is strongly dependent on x_c but this effect is also greatly diminished below T_{ni} since here $q(T)$ is reduced to very small values regardless of x_c (see Figure 2).

A parameter of great influence is the characteristic temperature T^*_i of isotropic interaction, i.e., the interaction parameter χ. Poor solvent quality of the liquid crystal for the polymer chains of the network will obviously diminish the swelling already above T_{ni}. A calculation using $\kappa = 10$

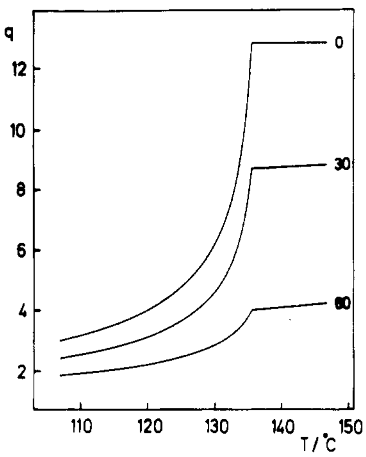

Figure 3. Degree of swelling $q(T) = V/V_0$ as a function of temperature. The calculation presented has been done for poly(butadiene) networks characterized by x_c = 300 (number of segments per linear chain) and κ = 10 (cf. Figure 1) immersed in the nematic liquid crystal PAA (for the characteristic data of PAA, see text). Parameter of the curves is the characteristic temperature T^*_i of isotropic interaction (cf. eq 6). It measures the solvent power of the liquid crystal for the poly(butadiene) chains.

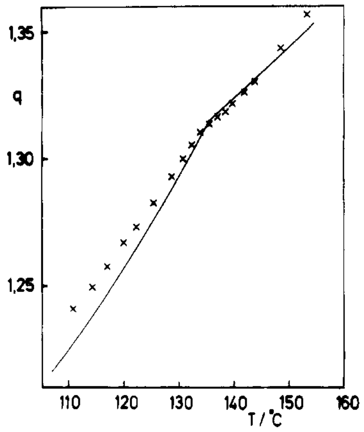

Figure 4. Experimental swelling curve of a poly(butadiene) network (x_c = 178; cf. eq 15 and Figure 2) in the nematic liquid crystal PAA: crosses, experimental result; solid line, theoretical result for $q(T)$. The characteristic temperature T^*_i of isotropic interaction (cf. eq 6) necessary for the fit is 129.5 K; κ = 10 (cf. Figure 1); all other characteristic parameters of the network and the liquid crystal are as given in the text.

and x_c = 300 displayed in Figure 3 shows indeed that for the present set of parameters $q(T)$ may assume rather small values even if the network is immersed in the isotropic phase of the liquid crystal. The anomaly of $q(T)$ at T_{ni} may be hard to detect in this case.

To test the foregoing predictions, poly(butadiene) networks were immersed in PAA and EBBA. Figure 4 displays the experimental result for a network swollen in PAA.

From a comparison of Figure 4 with Figure 3 it is obvious that PAA is a rather poor solvent since the degree of swelling in the isotropic phase hardly exceeds unity. In addition to this, q strongly depends on temperature, which is furthermore indicative of an unfavorable isotropic interaction between the flexible polymer and the swelling agent. For a quantitative comparison T^*_i is varied for κ = 10 until $q(T)$ calculated from theory describes the experimental data in the isotropic regime. The resulting value of T^*_i is rather high (129.5 K) and indicates the unfavorable network–solvent interaction. This effect and the high transition temperature of PAA, which leads to difficulties because of degradation of the network, makes a comparison of theory and experiment difficult. The anomaly of $q(T)$ at the transition point is clearly discernible, however.

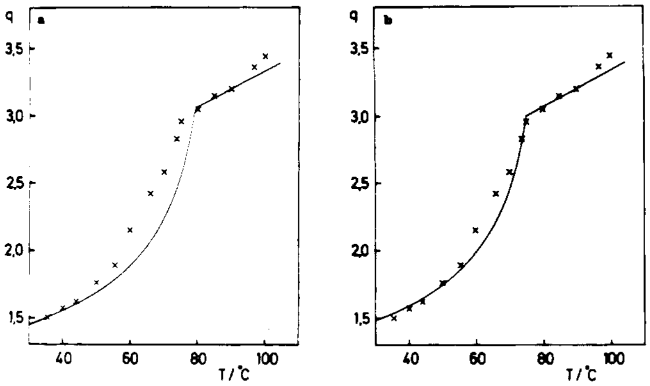

Figure 5. Experimental swelling curve of a poly(butadiene) network (x_c = 158; cf. eq 15 and Figure 2) in the nematic liquid crystal EBBA: crosses, experimental result; solid line, theoretical result for $q(T)$. The characteristic temperature T^*_i of isotropic interaction (cf. eq 6) necessary for the fit is 52.5 K; κ = 10 (cf. Figure 1). (a) All other characteristic parameters of the network and the liquid crystal are as given in the text. (b) All characteristic parameters are as indicated in the text and in a except T^*, which has been adjusted to 345.6 K to match the observed transition temperature (see text for further explanation).

More conclusive data can be obtained by using EBBA as a swelling agent. The experimental $q(T)$ values together with the respective theoretical curves are displayed in Figure 5. In Figure 5a only T^*_i (52.5 K) has been adjusted (κ = 10) to reproduce the slope in the isotropic phase. The much smaller value of T^*_i leads to a much higher uptake of solvent (cf. Figure 3). Qualitative agreement of theory and experiment is obtained.

For a quantitative comparison of theory and experiment it has to be noted that T_{ni} is lowered somewhat due to unavoidable impurities in the system. Adjusting T_{ni} in the system to the temperature where $q(T)$ changes its slope, the theoretical $q(T)$ may be fitted to the experimental result. First T^*_i is adjusted until the slope of $q(T)$ in the isotropic phase is reproduced. Then the characteristic temperature of anisotropic interaction T^* of the liquid crystal is lowered by a few degrees to match the lower transition point in the system. The $q(T)$ curve (cf. Figure 5b) thus obtained describes the experimental result quantitatively within experimental uncertainty.

Conclusion

The foregoing comparison of theory and experiment has clearly shown that theory is able to explain all the experimental features of $q(T)$ with a minimum of adjustable parameters. The present experiments corroborate the Flory–Rehner hypothesis. For a more stringent test of this assumption the fit parameters T^*_i must be measured independently. In principle, T^*_i would be available from solutions of linear poly(butadiene) in the respective liquid crystals. Also, the stress–strain curve of the network measured in the dry state would provide an independent source for the parameter κ. Experiments conducted along these lines will allow an even more stringent test of theory. It is questionable, however, whether the present systems are suitable for a more detailed comparison of theory and experiment since poly(butadiene) is quite susceptible to degradation at higher temperatures. Networks composed of siloxane chains would probably be the material of choice for a further test of theory.

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