SANS Experiments on Swollen Mesomorphous Networks

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ABSTRACT: The structure of mesomorphous elastomers, made of cross-linked side-chain liquid crystal polymers, is investigated by small-angle neutron scattering. Three types of samples are synthesized in the presence of deuterated toluene, one without mesogenic groups (C) and two with different proportions of pending mesogenic side chains (A and B). SANS is measured at the preparation concentration state and at maximum swelling, in equilibrium with deuterated solvent. These experiments give a test of the homogeneity of cross-linking. Samples carrying bulky mesogenic side groups (A and B) appear to be less heterogeneous than the corresponding mesogen-free network (C). Results are discussed in terms of mesomorphous interactions which are still present at the preparation swelling ratio and in terms of a steric effect due to the side chains, which prevents chains from interpenetrating and entangling.

1. Introduction

In the past few years, cross-linked side-chain liquid crystalline polymers have attracted considerable attention.[1−6] These materials are composed of polymer backbones, essentially polyacrylate or polysiloxane, bearing pendent mesogenic groups, and chemically linked together either by flexible chains or by mesogenic-like cross-links. These compounds exhibit exceptional properties, due to the combination of elastic properties and mesomorphous behavior.[7,8] Like conventional elastomers, they can sustain large deformations causing molecular extension and orientation. Furthermore, they can exhibit spontaneous distortions, memory effects, and unusual mechanical responses. The coupling between an optical or an electric field with an imposed mechanical field is of great interest, both for the physics it involves and for technological applications. All these properties have been widely studied in recent years. Nevertheless, the microscopic structure of these materials is not, at this time, well-defined, and the question of the homogeneity of the distribution of the linkages remains open.

One reference material for liquid crystalline polymer networks is, of course, networks of usual polymers. In such materials, it is known that the spatial distribution of the modulus (and probably of the density of cross-links) is not homogeneous but instead displays a structure that is considered a characteristic of the network. This could be in particular underlined by the heterogeneity of solvent concentration, when the network is swollen in a solvent of the chains. Such fluctuations of concentration can be analyzed via radiation scattering; small-angle neutron scattering (SANS) of samples swollen by a labeled solvent is appropriate for distances between 10 and 1000 Å, where heterogeneities are often visible. This is the case for polystyrene networks,[9] prepared by different methods (random cross-linking of large chains, anionic networks, end-linked networks) in solution, and for PDMS networks made from a melt.[10] Other gels have been observed by neutron, light, or X-ray scattering.[11] All networks exhibit heterogeneities and can display one or two different correlation lengths, some fractal behavior, or a correlation peak. It clearly depends on the type of gels, mostly on its conditions of preparation.

Concerning liquid crystalline polymer networks, the distribution of the linkages is worth further study: on one hand, in these materials (which are obtained either in bulk or in concentrated solution using a cross-linking agent which is generally incompatible with both liquid crystalline groups and backbone), some specific interactions between mesogens could induce a microsegregation phenomenon, for example. Moreover, the chains are very short; the yield of the cross-linking reaction could be lower than expected, which could lead to very heterogeneous networks such as those observed close to a gelation threshold. On the other hand, the presence of the large pending groups could reduce any possibility of trapped entanglements and even any interpenetration. A naive idea would then be that the networks could be more homogeneous, because the different strands could pack closely to each other, thus reproducing a relatively regular structure of a net of strands. There are also possible interactions between the mesogenic pending moieties. For example, a trend toward nematic or smectic order could be present. This onset of order could reduce the degree of heterogeneity and restrict it to a correlation at a finite value of q.

In this paper, we present experimental results obtained on samples swollen by labeled solvent. Two mesomorphic samples with different proportions of liquid crystalline pendent groups were synthesized. The elastomers under study were prepared in the presence of deuterated toluene, and two swelling states were successively studied by SANS: the first one corresponded to the concentration of preparation, and the second state consisted of the maximum swelling that the network can undergo. In the latter state, possible heterogeneities were enhanced.[9] Results obtained on the mesomorphous networks were compared with those obtained on a similar mesogen-free elastomer. Any physical system is heterogeneous, at least at a certain

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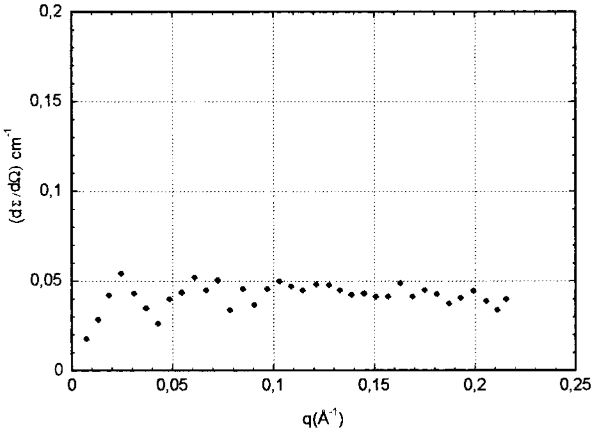
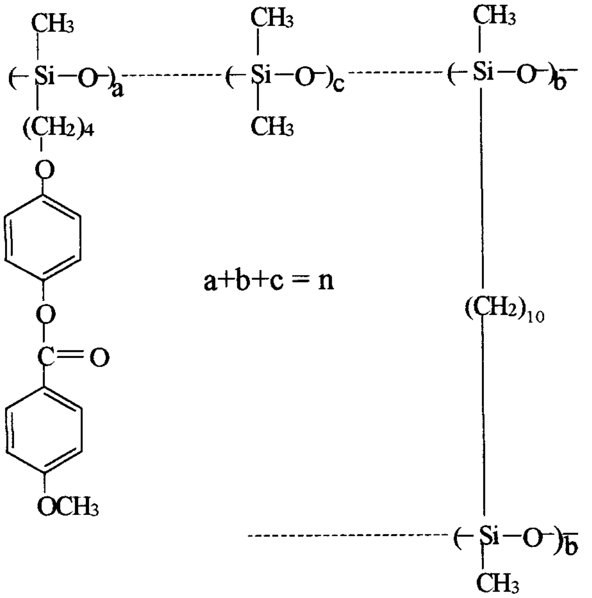


Figure 1. Neutron intensity scattered by an undiluted copolymer containing 55% of hydrogen methylsiloxane units and 45% of perdeuterated dimethylsiloxane units (q: scattering vector amplitude).

scale; we characterized this scale by a correlation length (ξ), a correlated volume (ξ^3), and a certain amplitude.

2. Experimental Section

2.1. Sample Preparation and Characterization. The networks investigated have the following general formula:



The precursor polymer backbone was either a commercially available poly(hydrogen methylsiloxane) from Petrach (sample A) or poly(hydrogen methylsiloxane-*co*-dimethylsiloxane)s, with respectively 5% (sample C) and 55% (sample B) of hydrogen methylsiloxane units, synthesized in the laboratory as previously described.[12] The average number molecular weight of the three polymers was determined by tonometry experiments and corresponded to an average number degree of polymerization (n) of 90 units. The polydispersity, characterized by means of gel permeation chromatography (GPC), was relatively narrow ($M_w/M_n = 1.3$). For copolymers, the random distribution of the units was checked[12] by ^{29}Si NMR and, for one of them, by SANS. This latter technique was performed on a copolymer containing 55% of hydrogen methylsiloxane units and 45% of perdeuterated dimethylsiloxane units (deuterated analogue of the backbone used for sample B). The scattered intensity (coherent part, Figure 1) showed no structure in q (the graph was flat). Thus, there was no concentration fluctuation of one species with respect to the other. This confirmed that in the q range explored ($4 \times 10^{-2} < q$ (Å^{-1}) $< 2.2 \times 10^{-1}$) the distribution of dimethylsiloxane and hydrogen methylsiloxane units was statistical.

Mesogenic groups, ended by a vinyl group, were synthesized as previously described.[13] The cross-linking agent was a commercially available 1,9-decadiene. Samples were prepared in solution by a one-step hydrosilylation reaction between the hydrogen methylsiloxane units and the vinyl end groups of either the mesogens or the linkages.[5,14] The proportions of cross-links and mesogens indicated in Table 1 were deduced from the respective proportions introduced during synthesis without referring to any effective cross-linking. The reaction was performed in perdeuterated toluene. During synthesis, the concentration was rigorously kept to 37 vol % of polymer chains. All the elastomers were prepared under the same conditions, and the adopted synthesis conditions created samples with no particular macroscopic orientation of the mesogens. These samples were ready for SANS at the concentration of preparation.

In the dry state, compounds A and B exhibited mesomorphous phases whose nematic or lamellar structure was analyzed by X-ray scattering. Their transition temperatures, determined by differential scanning calorimetry, are given in Table 1. The smectic A structure was established by two-dimensional X-ray measurements taken on samples orientated by mechanical stretching.[15]

Gels can be overswollen with respect to the preparation conditions. Samples prepared in d-toluene were put in a large excess of d-toluene and swollen to saturation in order to reach their maximum swelling ratio (Table 1).

2.2. Neutron Scattering Experimental Setup. SANS experiments were performed on the "P.A.X.E" instrument at the Léon Brillouin laboratory (Saclay). Two configurations were used: the first one used an incident wavelength of 10 Å and a sample detector distance, L, of 3.20 m, giving a q range of $4.3 \times 10^{-3} < q$ (Å^{-1}) $< 7 \times 10^{-2}$, and the second used an incident wavelength of 6.5 Å and $L = 1.60$ m; the q range covered was $1.3 \times 10^{-2} < q$ (Å^{-1}) $< 2.2 \times 10^{-1}$. Standard corrections for detector response and cell windows scattering were applied to obtain the intensity scattered, the scattering cross section, and $I_{\mathrm{sample}}(q) = \mathrm{d}\epsilon/\mathrm{d}\Omega(q)$ (cm^{-1}) from the sample.[16]

The units are equal to absolute units, i.e., cm^{-1}, within ±20%.

Incoherent scattering, calculated as a combination of incoherent scattering from pure solvent and from pure (undiluted) non deuterated polymer melt, was subtracted from $I_{\mathrm{sample}}(q)$ to give the coherent scattering.

3. Results

3.1. Mesogen-Free Network. We discuss below data between 0.01 and 0.1 Å^{-1} corresponding to the superposition of the data obtained from the two configurations, except for the smallest q of the low-q configuration.

In Figure 2 are plotted the cross sections $\mathrm{d}\Sigma/\mathrm{d}\Omega$ versus the scattering vector q, on a log−log scale, for the sample C in d-toluene, at two swelling ratios: the one corresponding to the concentration of preparation ($\phi_{\mathrm{prep}} = 0.37$, i.e., $Q_{\mathrm{prep}} = 2.7$) and the other one for equilibrium swelling ($\phi_{\mathrm{eq}} = 0.15$, i.e., $Q_{\mathrm{eq}} = 6.6$). Q and ϕ are the volume swelling ratio and the volume fraction of polymer, respectively. In both cases the signal is remarkably flat at the low q's (except below 0.01 Å^{-1}, for which the intensity slightly increases for $q \to 0$) and is very close to a single Lorentzian behavior as underlined in Figure 3:

$$\mathrm{d}\Sigma/\mathrm{d}\Omega\ (\mathrm{cm}^{-1}) = I_0/(1 + q^2\xi^2) \qquad q\xi < 1 \qquad (1)$$

For a semidilute solution, we have the same expression, where ξ is the size of the excluded volume blob, i.e., the typical distance between two interchain contacts.

Table 1. Characterization of the Networks

	composition %			thermal transitions in dry samples (°C)							swelling ratio[b]	
sample	*a*/*n*	*b*/*n*	*c*/*n*	T_g	S_A		N		I	dS_A[a] (Å)	Q_{prep}[c]	Q_{eq}[d]
A	90	10	0	9	•	55	•	78	•	34	2.7	6.1
B	45	10	45	−13	•	30			•	42	2.7	6.6
C	0	5	95	−120							2.7	6.6

[a] Layer spacing in the smectic A phase. [b] Volume ratio of the swollen network in perdeuterated toluene upon the dry network. [c] Q_{prep}: in the reaction bath. [d] Q_{eq}: in a large excess of solvent.

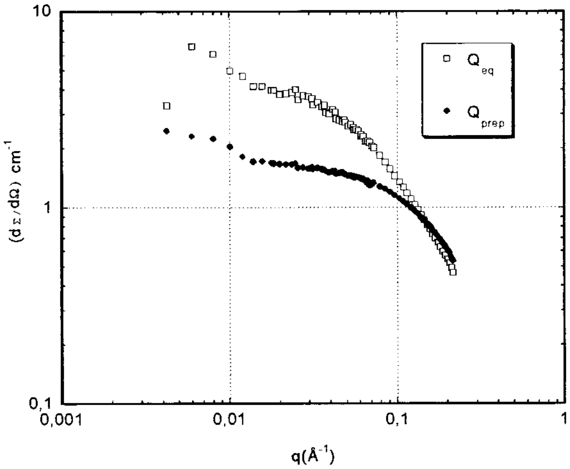


Figure 2. Log−log plot of the intensities scattered by mesogen-free swollen network. Q_{prep} is the network swollen at the concentration of the reaction bath. Q_{eq} is the network swollen to saturation.

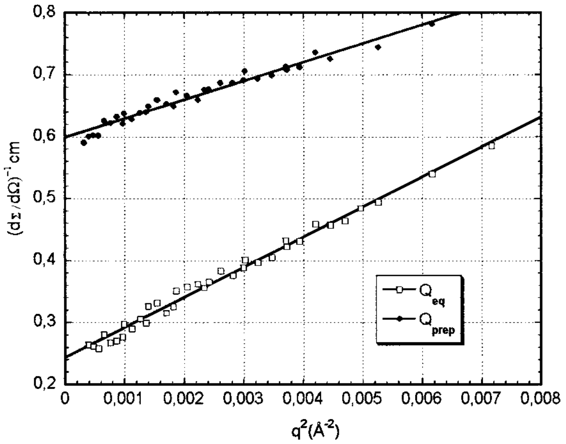


Figure 3. Inverse of the scattered intensity versus q^2 for mesogen-free swollen network.

At very large *q*'s, one would imagine to see the inside of the chain between cross-links, which is expected to show, as in a semidilute solution, excluded volume statistics, i.e., a variation in $q^{-1/\nu} = q^{-1.6}$ ($\nu = 3/5$). However, a typical strand between two cross-links is expected to be very short (20 units). Thus, such a $q^{-1.6}$ behavior should occur in a *q* range larger than the one covered here. This is probably why we only observe the beginning of the curve and why the apparent slope is lower than expected (around −1.4 instead of −1.6).

Returning to the low-*q* regime, the correlation length (ξ) and the zero-*q* limit of the intensity scattered (I_0) can be determined (Figure 3):

$$\text{for } Q_{prep} = 2.7,\ \xi = 7\ \text{Å, and } I_0 = 1.66\ \text{cm}^{-1}$$

$$\text{for } Q_{eq} = 6.6,\ \xi = 14\ \text{Å, and } I_0 = 4\ \text{cm}^{-1}$$

With only these two ξ values, we can estimate the apparent exponent α assuming a power law $\xi = k\phi^{-\alpha}$; we find $\alpha = 0.78$. For a semidilute solution in good solvent, α is equal to 0.77: dilution progressively increases the size at which the chains are interpenetrated. The same phenomenon could occur here if the chains are interpenetrated at scales shorter than the average distance between cross-links. Alternatively, the blob size could be locked on this distance; assuming affine displacement of the junction during swelling would give $\xi = k\phi^{-1/3}$, i.e., $\alpha = 1/3$.[9] Various values larger than 0.77 have been observed,[9,10] up to 5/3. This behavior has been attributed to progressive disinterpenetration of the regions of larger cross-linking density. The value of 5/3 can be explained by mapping the problem as one of dilution of percolation clusters.[17]

In our case we keep close to a simple deinterpenetration, as in a semidilute solution. This is surprising, since the cross-linking ratio is high. Thus, several cross-links should exist in a volume equivalent to the one of a blob of a semidilute solution, which would hinder deinterpenetration.

For a semidilute solution in good solvent, I_0 is given by

$$I_0 = AK^2\phi^2\xi^3 \tag{2}$$

where $A = 1$ within ±20% (see above) and *K* (cm^{-2}) is the difference in density of scattering length between the solvent and the polymer. This gives $I_0 = k\phi^{-\beta}$ with $\beta = 2 - 3(0.77) = -0.31$. We find here $\beta = -0.98$, meaning that the relation $I_0 = k\phi^2\xi^3$, which should lead to $\beta = 0.31$, is not obeyed here. Thus, even if the correlation length varies with $\phi^{-0.78}$, the mechanism of dilution is different from a semidilute solution but does not show a very strong dependence on ϕ as would be obtained with strong fractal-like heterogeneities. It is also very far from affine swelling: the intensity would be proportional to ϕ, instead of $\phi^{-0.98}$ here!

Moreover, the values of ξ show very moderate sizes for such heterogeneities. This, added to the lack of low *q* upturn (at least down to 0.01 Å^{-1}), makes us conclude that these networks are not very heterogeneous at this scale. The cross-linking method does not introduce strong constraints in the system. One should relate it to the fact that the expected cross-linking ratio, one for 20 monomers (5%), is large. However, the equilibrium swelling ratio values are higher than the ones expected from the Flory−Rehner theory of swelling. This agrees with the values of only 0.2 MPa obtained for the *G* elastic modulus (see sample named “E4” in ref 14). This value corresponds to around $n_e = 200$ units between junctions, using the classical expression for the modulus of a network, i.e., $G = \rho RT/mn_e$, ρ (mg/cm^3) being the density and *m* the mass of the unit.[18]

In summary, as for linear polymers, networks under swelling display some increase of the correlation length

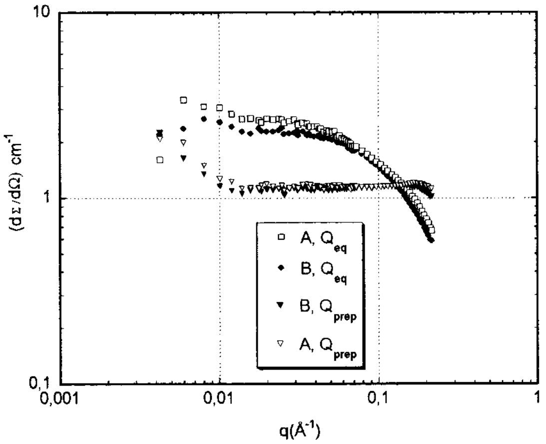


Figure 4. Log–log plot of the intensities scattered by mesogenic swollen networks. Q_{prep} is the networks swollen at the concentration of the reaction bath. Q_{eq} is the networks swollen to saturation.

and of the zero-q limit of the intensity scattered; this increase is contradictory to a theory of affine swelling as for usual networks. Compared with dilution of a semidilute solution, the increase is stronger for the zero-q intensity but identical for the correlation length. Thus, though heterogeneities are also present in these networks, the latter are relatively homogeneous at the scale for SANS. Though the cross-linking is not totally effective, the synthesis method does not create extremely perturbative heterogeneities, at least compared to other networks.

3.2. Mesogenic Networks. We now observe the cross section of samples A and B, containing mesogenic units, swollen in d-toluene at the concentration of preparation and at maximum (equilibrium) swelling. Compared to the former sample C, the difference is striking, in particular for Q_{prep}. The log–log plot (Figure 4) consists, for both samples, of a very low ($I_0 = 1.1$ cm^{-1}) and flat line, with a weak maximum at the largest q. The information from the low q range is clear: the correlation length is very small. Upon further examination, it is probable that one can describe the curve as the sum of a Lorentzian, which would start to decrease above $q = 0.1$ Å^{-1}, i.e., ξ around 5 Å, and a wide bump. This bump could be the signature of the smectic lamellar structure of these networks which seems to be preserved in the presence of solvent at this state of swelling. The maxima observed for swollen samples A and B are respectively around 34 and 44 Å, close to the S_A layer thickness determined in the dry state (see Table 1).

At the concentration of equilibrium swelling, this large q maximum vanishes, and one is left with a Lorentzian behavior again. Here also there are no additional heterogeneities at very low q. Figure 5 allows us to determine

for sample A ($Q_{\mathrm{eq}} = 6.1$):

$$\xi = 9 \text{ Å and } I_0 = 2.74 \text{ cm}^{-1}$$

for sample B ($Q_{\mathrm{eq}} = 6.6$):

$$\xi = 8 \text{ Å and } I_0 = 2.35 \text{ cm}^{-1}$$

Apparently, no important effect of the mesogenic groups proportion can be seen. However, one can note that the largest values of ξ and I_0 are obtained for sample A, which has the lowest swelling ratio. Thus, although the global effect of the mesogens is to reduce the scattering, sample A, which has more mesogens, scatters more (i.e., appears slightly more heterogeneous) than sample B. However, the difference between samples A and B is perhaps not very significant: while the fraction in number of mesogens is divided by a factor of 2 (0.90 against 0.45) from sample A to sample B, the volume fraction occupied by the mesogens, evaluated at the dry state, varies only from 0.8 to 0.7.

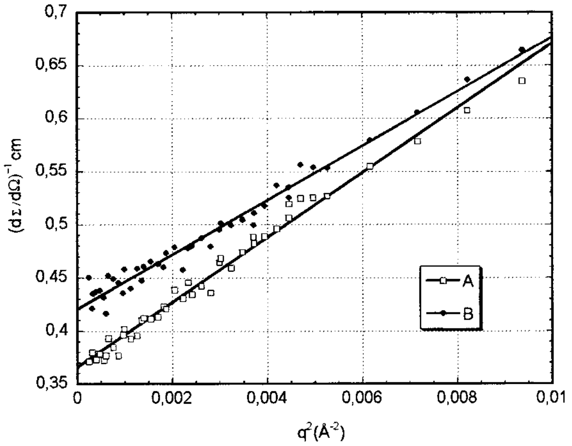


Figure 5. Inverse of the scattered intensity versus q^2 for mesogenic networks swollen to saturation.

Assuming $\xi = 5$ Å at the concentration of preparation, from the ratio of the ξ's and I_0's, we can give a rough estimate of the exponents close to those obtained for the mesogen-free sample (for example, for sample B $\alpha = 0.65$ and $\beta = 1.02$). However, a clear difference lies in the absolute values: the values for $Q > 6$ for these samples are similar to those observed in the case of the mesogen-free sample for a swelling ratio Q of only 2.7. So, adding pending groups at the same time as cross-linking the chains reduces the heterogeneity of the network.

4. Summary and Conclusion

We have investigated the degree of heterogeneity in swollen networks made from short precursor chains, by chemical addition of cross-links only or by addition of both cross-links and mesogenic units. This last synthesis was developed in order to produce liquid crystal networks after drying without particular macroscopic orientation of the mesogens. The samples were observed at two degrees of swelling in deuterated toluene with respect to the dry state: one corresponding to the concentration of preparation and the second one at the concentration of equilibrium swelling, i.e., corresponding to overswelling with respect to the preparation state.

We characterized the degree of heterogeneity by a ξ correlation length. In all cases, ξ increased with swelling and did not follow the variation predicted by affine swelling theories, as already well established for other polymer networks. The dependence on the concentration was not very different from the one of semidilute solutions in good solvent. The zero-q limit of the intensity scattered was another parameter of the degree of heterogeneity that was examined; it also increased under swelling, again contrary to the affine swelling model, which again was observed for other networks. The dependence on the concentration was different from the one of semidilute solutions in good solvent, i.e., notably stronger. The variation remained reasonable however. For the mesogen-free sample, the correlation lengths varied between 7 and 14 Å. For mesogenic samples, the values were extremely low at the concentration of preparation (around 5 Å) and still low at maximum swelling (8−9 Å). We therefore reached an important conclusion: the mesogenic networks appear rather homogeneous. Such apparent homogeneity was reassuring: we feared that the advantages of making liquid crystalline samples would result in a network of poorer quality. For example, it seems that equilibrium swelling ratios, as well as moduli previously measured,[14] signal a rather low efficiency of cross-linking. But this was not the case at the level of spatial distribution of the cross-links: the addition of mesogenic parts reduced the heterogeneity of the sample. A priori there are two reasons for that: (i) the liquid crystalline order (smectic), which seems to be established at the concentration state (see the correlation peak in Figure 4), and (ii) the additional volume brought to the chains by the mesogenic pending parts.

The role of such a steric effect is not passive:[19] it may reduce cross-linking heterogeneities during the formation of the network, because cross-linking heterogeneities would create larger fluctuations of concentration if the chain bears more mass (mesogens). These larger fluctuations would be expensive in terms of free energy. In a slightly different but more direct point of view, the steric effect should prevent two chains from interpenetrating and entangling. However, in this line of thought, we have to remark that steric effect can (ii.a) act during the gelation (i.e., the building of the network), giving a less heterogeneous network (preventing cross-linking heterogeneity), and (ii.b) act only after the gelation: then even if the network is inhomogeneous, swelling cannot reveal it because of the steric effect.

Though it seems to us that the assumption of additional volume effect (ii.a) is the most robust and that liquid crystalline order (i) is not as important, it remains to establish which is the dominant origin.

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(19) One could think that the role of such volume is only passive; the pending part would bring more volume and thus reduce the fluctuations as each time the concentration of a solution is increased. However, this effect is included in the quantity Q, the global volume swelling (if only the polymer backbones were visible, they would look more dilute than for a mesogen-free network at the same volume swelling Q).

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