

Structure and swelling of polymer networks: insights from NMR

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This review addresses the relationship between the structure of elastomers and gels, *i.e.*, polymer networks far above the glass transition, and their macroscopic properties. The network structure is characterized by the density of crosslinks, the chain length distribution, topological defects, and entanglement effects, and can be tuned by varying the preparation conditions. These quantities ultimately determine the functional (mostly mechanical) properties, and sensitively affect the swelling behavior. Here, we review current efforts using different NMR spectroscopy methods to unravel structural details of various networks made from poly(dimethylsiloxane), and correlate these with their swelling behavior in solvents of different quality. It was found that a specific NMR observable based upon segmental orientation correlations reflects not only the network chain structure, but also the thermodynamic state. This allowed us to draw relevant conclusions on the validity of the Flory–Rehner theory for network swelling, and on the applicability of simple models to describe network elasticity.

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I Introduction

Polymer networks in their entropically elastic state far above the glass transition in the bulk or in a swollen state as gel have many relevant applications, *e.g.* as rubber materials, separation membranes, or cell culture media, to name just a few. The

relevant properties of these materials depend on their molecular properties, *i.e.*, the molecular weight between crosslinks M_c , the overall topology mainly characterized by the crosslink functionality f , spatial inhomogeneities, and the fraction of elastically inactive material ω_{def} (henceforth referred to as defects, comprising dangling chains and loop structures), and finally the sol fraction ω_{sol} (unconnected polymer chains). Since networks cannot be dissolved but only be swollen, their exact characterization poses specific challenges. The above-mentioned quantities, in particular M_c or its inverse, and the density of crosslinks or crosslinked chains $n \propto 1/M_c$ can of course be indirectly inferred from the elasticity modulus or the equilibrium degree of swelling using well-established but still controversially discussed theories, such as the affine network model of Flory and Wall,^{1,2} the phantom model by James and Guth,³ or various extensions of these,^{4,5} to describe elasticity. The still most popular theory for swelling is the Flory–Rehner (FR) theory,⁶ which assumes additivity and independence of the osmotic effect driving the solvent uptake, described by simple Flory–Huggins (FH) theory, and the elastic restoring force.

Decades of research have revealed substantial shortcomings of the above-mentioned theories. Scattering experiments have shown strongly non-affine deformation on local scales and strong swelling inhomogeneities,^{7,8} and numerous thermodynamic studies stressed anomalies, in particular for partially swollen networks.^{9–12} Even though the most striking and intensely discussed anomaly, the minimum of the osmotic modulus, has just recently been identified as a possible artefact of the necessary data smoothing,¹² the simple FR theory cannot account for this quantity not being a constant. Still, ad-hoc concentration or crosslinking dependencies of the FH

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setts (Amherst, USA) working with K. Schmidt-Rohr, his continuing research interest has been the development and application of NMR techniques to the study of structure and dynamics in polymeric, liquid-crystalline, and other 'soft' materials, which have been published in about 90 papers.

interaction parameter χ describing the enthalpic contributions to the mixing thermodynamics must be assumed.^{11–17} In these and related works it is already realized that the (apparent) crosslink dependence of the χ parameter is most likely due to the failure of the additivity assumption mentioned above, and of course the use of the after all simplistic FH theory as opposed to a more precise equation-of-state approach.

NMR studies of networks, elastomers and gels have been pioneered by Cohen-Addad,^{18,19} who has discovered the basic principles¹⁸ and has published many applications in particular to swollen systems that form the basis of the work addressed in this review.¹⁹ Significant methodological refinements are due to Callaghan and Samulski,²⁰ who for instance clarified the role of entanglements for network elasticity.²¹ In addition, earlier NMR results have already led to suggestions for the improvement of theories for network elasticity, stressing the role of orientation correlations arising from excluded-volume interactions.²²

In recent years, work in our group has stressed the use of NMR spectroscopy, and in particular of a specific ^1H low-field NMR technique dubbed double-quantum (DQ) NMR as the most quantitative tool to date to characterize the network structure.²³ This and the other mentioned NMR approaches rely on the through-space ^1H – ^1H dipole–dipole coupling within monomer units, which is orientation dependent and thus reflects the amplitude of orientation fluctuations of the chain segments. Since these are not fully isotropic in network chains suspended between two fixed ends (crosslinks), a finite residual dipolar coupling D_{res} persists for segments in network chains,¹⁸ but not in elastically inactive, isotropically mobile chains (defects and sol). D_{res} is the primary observable, and it is proportional to a dynamic chain order parameter S ,

$$D_{\text{res}} \propto S = \frac{1}{2} \left[3 \langle \cos^2(\theta) \rangle - 1 \right] = \frac{3}{5} \frac{l^2 R^2}{R_0^4} \stackrel{(\text{Gauss})}{=} \frac{3}{5N} \left(\frac{R}{R_0} \right)^2, \quad (1)$$

where $\langle \dots \rangle$ denotes the thermal average over all conformations of a network chain and $[\dots]$ denotes the structural average over all segments in the sample. The angle θ refers to the instantaneous segmental orientation with respect to the end-to-end vector of the given chain (see the inset of Fig. 2b below). Our method can not only reliably determine the average S , but also its distribution in an inhomogeneous sample.^{23,24} The technique yields, as the second main result, also the fraction of network defects ω_{def} .

As is reflected by the right hand side of eqn (1) which is valid for Gaussian statistics (in the bulk or θ solvent), S depends on the number of segments (ultimately monomers) N in the network chains, thus M_c , and also on its state of stretching *via* the normalized end-to-end distance R/R_0 . In general, the ratio R^2/R_0^4 makes this observable also sensitive to the thermodynamics of the swollen network, as discovered recently.^{25,26} In fact, the theory provides a direct relationship between the order parameter S and the conformational properties of the network strands including solvent effects.^{25,27}

We have used our NMR technique to tackle a number of questions in network and rubber science.²⁸ Specifically, we

could earlier prove qualitatively the existence of swelling heterogeneities and strongly non-affine stretching of network chains on a molecular level.²⁹ This highlight review focusses on more recent work exploiting the mentioned NMR technique in two directions, first, using its potential to quantify the network structure in evaluating the validity of classical elasticity theories by comparing with the results of swelling experiments and an alternative, independent and unbiased assessment of the network structure,³⁰ and second, to use its sensitivity to the thermodynamic state of swollen networks *via* the sensitivity to R^2/R_0^4 to critically discuss the validity of the Flory–Rehner (FR) theory.²⁶ This review provides the backdrop to the current work on characterizing states of intermediate swelling below equilibrium in networks prepared in the bulk and in the solution state, published in this issue of *Soft Matter*.³¹

II Evidence for phantom behavior from NMR and swelling experiments

For a critical evaluation of theories for network swelling it is most desirable to work with networks of a precisely known structure. For this purpose, the so-called “model networks” prepared by end-crosslinking reactions of well-defined prepolymers have been studied intensely. However, these systems suffer from a particularly large amount of defects³⁰ such as loops formed by chains with two ends attached to the same crosslink. We have therefore studied statistically crosslinked networks based on linear PDMS precursor polymers with $M_w \approx 30$ kDa with variable amounts of vinyl-containing comonomers and variable amounts of bifunctional linker molecules determining the reaction turnover. The latter can be precisely determined by suitable integration of simple high-resolution ^1H MAS NMR spectra of the elastomers, see Fig. 1a. Our networks also exhibit rather large defect fractions ω_{def} in particular at low turnovers. However, the ω_{def} can be measured by our DQ NMR technique. As is shown in Fig. 1b, the correct ω_{def} is obtained only from measurements in swollen samples, while a part of ω_{def} appears elastically active in bulk samples. The associated relaxation time into a state of isotropic orientation distribution is obviously longer than the timescale of the NMR technique ($\sim 10^{-3}$ s), and suggests an influence on the time-dependent mechanical properties, as observed in similar networks.³² The elucidation of the origin of the pseudo-elastic response of the defects is also addressed in ref. 31 in this issue.

The advantage of our sample series is that the network structure, *i.e.* the average M_c , can be calculated quantitatively using the statistical Miller–Macosko (MM) theory of crosslinking.³³ The input parameters to a suitable numerical implementation of the theory are the exact vinyl group contents and their conversion taken from high-resolution NMR, as well as the sol fraction from swelling experiments, ω_{sol} , and the known M_w and the polydispersities of the prepolymers. In this way, the theory predicts M_c , the weight-averaged effective functionality of the network f_{wa} which varies between 2 and 4 (Fig. 1b), and the (non-sol) defect fraction ω_{def} . As a convincing consistency test, we find the latter to be in quantitative agreement with our experimental findings. The

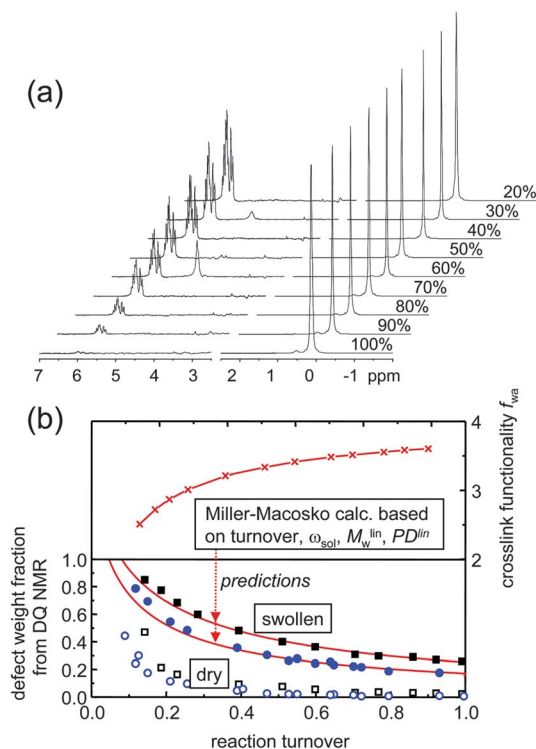


Fig. 1 (a) High-resolution ^1H MAS NMR spectra of a partially crosslinked, randomly vinyl-functionalized PDMS precursor polymer with variable reaction turnovers using a bifunctional linker. The olefinic region is amplified. The exact reaction turnover obtained by integration of the residual vinyl signal along with the sol fraction from extraction experiments, and M_w and the polydispersity PD of the linear precursors, is used to obtain the weight-averaged crosslink functionality f_{wa} shown in (b) on the basis of Miller–Macosko theory. The fraction of non-elastic defects obtained from DQ NMR experiments in the swollen state, see the lower part, is quantitatively reproduced by the theory. Squares and circles represent data for precursors with about 4 and 8 mol% of vinyl units, respectively. Data taken from ref. 30.

important advantage of our sample series is the variation in f_{wa} , which can be used to prove the validity of the phantom model.

Turning to the FR theory, swelling equilibrium is usually cast into a form equal or similar to

$$\ln(1 - \phi) + \phi + \frac{1}{2}\phi^2 - \frac{1}{2}v\phi^2 + ng_f\phi^{1/3} = 0. \quad (2)$$

Here, ϕ denotes the polymer volume fraction. The effective interaction parameter (second virial coefficient) is denoted by

$$v = \frac{1}{2}(1 - 2\chi) = B \frac{T - \theta}{T}, \quad (3)$$

and the first three terms in eqn (2) represent all higher-order virials. The last expression defines the θ -temperature, and B should be considered as the empirical parameter. The solution of eqn (2) provides the equilibrium degree of swelling $Q_{eq}(v, n g_f) = 1/\phi_{eq}(v, n g_f)$ as a function of temperature and effective crosslink density $n g_f$, where n is the number density of network strands $\sim 1/M_c$. Importantly, g_f depends on the elasticity model. Flory's affine model predicts $g_f = 1$, while the phantom model embodies an explicit dependence on f , $g_f =$

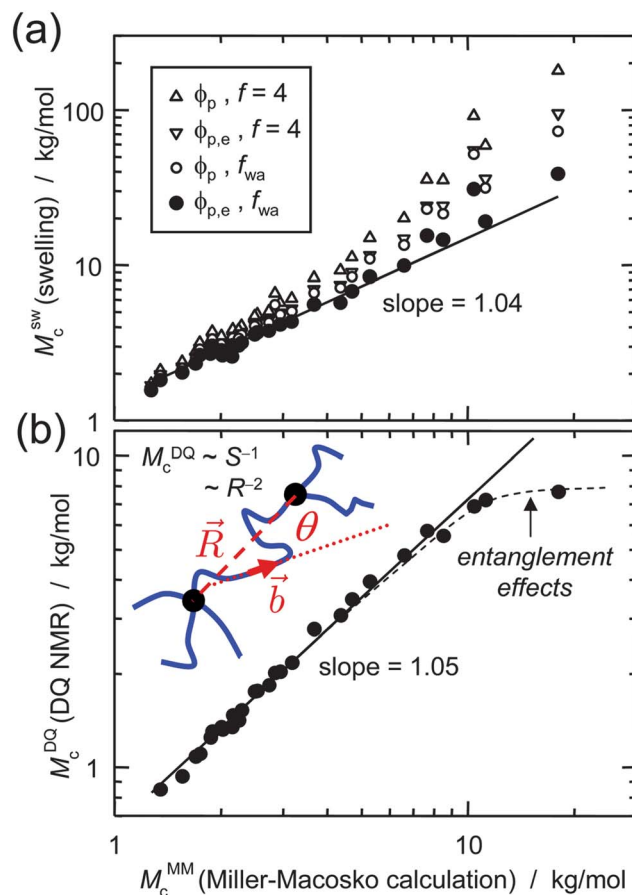


Fig. 2 Comparison of network chain molecular weights calibrated by Miller–Macosko calculations with the results from Flory–Rehner swelling experiments (a) and DQ NMR (b). The slopes in the log–log plots reveal that the best, near-linear correlation is only found if the weight-averaged crosslink functionality f_{wa} is taken into account, supporting the phantom model. For swelling, the polymer volume fraction ϕ_p further needs to be corrected for the NMR-detected amount of inelastic defects ($\Rightarrow \phi_{p,el}$ at swelling equilibrium). Data taken from ref. 30.

$(1 - 2/f)$, since the fluctuations of the crosslinks that provide an additional entropy contribution depend on their functionality. In a series of variable M_c and f , the two models can thus be distinguished.

The corresponding experimental results are shown in Fig. 2, where the values for M_c as obtained by the MM model are compared with the swelling results (a) and the values from DQ NMR (b). Clearly, the expected near-linear correlation is only found when the weight-averaged crosslink functionality f_{wa} is taken into account, providing clear evidence of phantom-type behavior. Another key point is that swelling results can only be considered quantitative when the defect fraction is subtracted before applying the FR eqn (2), and we stress that the exact defect fraction can only be measured on swollen samples with DQ NMR, or related and simpler transverse relaxation experiments. The $\sim 30\%$ absolute-value deviation between the MM- and NMR-results for M_c can be attributed to model dependencies on converting D_{res} in eqn (1) into N and then M_c .³⁴ Note that at large M_c , the NMR observable becomes dominated by the entanglement spacing M_e .

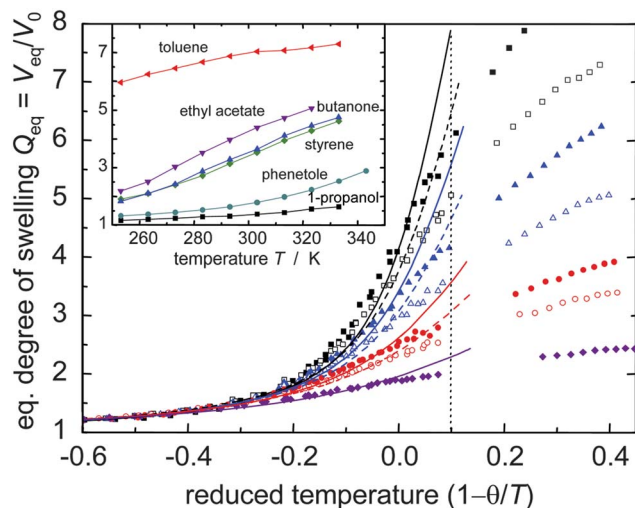


Fig. 3 Temperature-dependent degrees of swelling, $Q = 1/\phi_{p,eq}$, determined for a variety of PDMS-based networks in different solvents, combined into a master curve based on the assumed $1 - \theta/T$ temperature dependence of the second virial coefficient in Flory-Rehner theory. Styrene is taken as the reference solvent and θ is adjusted for all other solvents. The lines are fits to eqn (2). The inset shows temperature-dependent raw data. Data taken from ref. 26.

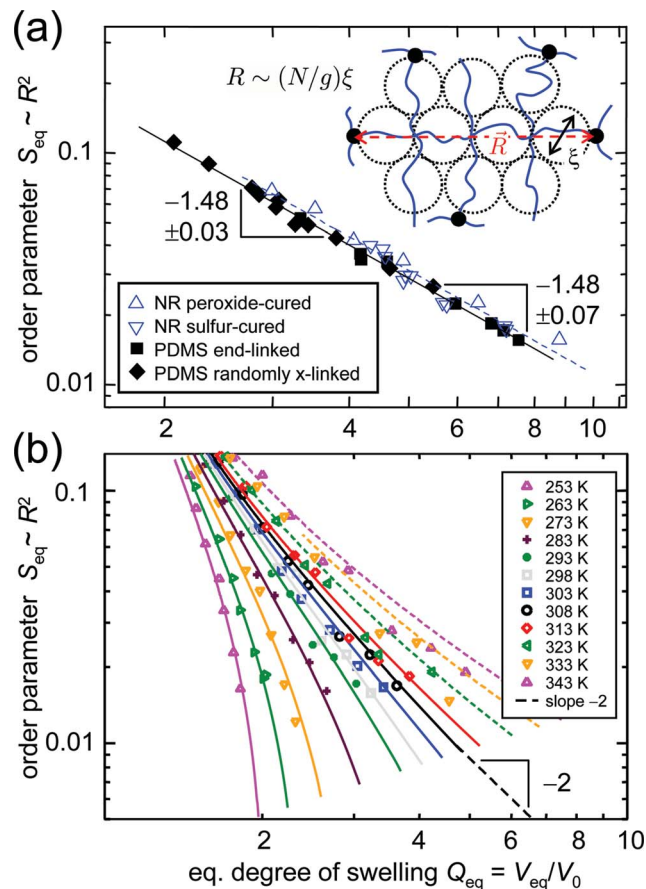


Fig. 5 Log-log correlation of DQ NMR-detected average segmental order parameters with the equilibrium degree of swelling for various networks in (a) good solvent and (b) the poor to good solvent range realized by swelling in styrene at different temperatures. The scaling exponent in (a) can only be explained by considering the blob model for semidilute solutions in good solvent, and shows that the use of simple (bulk) network chain entropy models is inappropriate for the swollen state. Data taken from ref. 25 and 26.

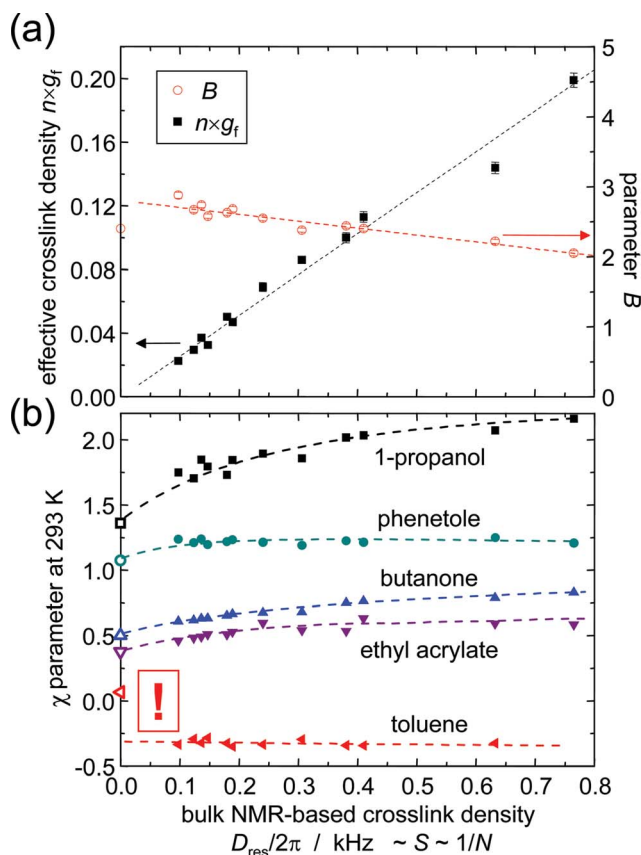


Fig. 4 Results from Flory-Rehner fits to the master curve data in Fig. 3 plotted vs. the DQ NMR measure of the average crosslink density of the different systems (D_{res} , which is proportional to $S \sim 1/N \sim 1/Mc$, see eqn (1)): (a) effective crosslink density $n \times g_f$ and prefactor B and (b) χ parameters calculated from B and the θ temperatures obtained from the shifting procedure. Data taken from ref. 26.

III Failure of Flory-Rehner theory for good solvents

Leaving NMR for a moment, the validity of eqn (2) can be scrutinized by temperature-dependent swelling experiments in solvents spanning a large range of effective χ parameters.²⁶ As is shown in Fig. 3, it is possible to construct “swelling master curves” by shifting the swelling data along the temperature axis, or as done in the figure, on the basis of a $1 - \theta/T$ temperature dependence. In matching suitably overlapping datasets, one can thus determine the θ temperature for a given network in a given solvent simply *via* the shift relative to a θ reference solvent, for which we chose styrene.

The so-obtained curves can be fitted with eqn (2) to yield the two parameters plotted in Fig. 4a. Note that the fits work well in a range below and around θ , while they fail to describe the bending-off in the good-solvent region. The results for the effective crosslink density and the empirical parameter B are convincing in that the former correlates perfectly linearly with DQ NMR results, while the latter is almost constant. This suggests that FR theory describes the swelling physics in the

poor to θ solvent range reasonably well. The major issue with FR theory as used for good solvents is apparent in Fig. 4b, where effective χ parameters are plotted, as calculated from eqn (3). We see a dependence on the crosslink density in agreement with many previous observations, and in the poor/ θ solvent range the results extrapolate well to the values known for solutions of linear PDMS (zero crosslink density). The back-extrapolation fails completely in the good-solvent range, and it is important to note that this observation is also true for the raw values for the effective θ temperatures obtained by the model-free shifting procedure. This suggests a fundamental problem of FR theory, which we elucidate in the following.

Turning to DQ NMR as a novel probe of network *thermodynamics* via the R^2/R_0^4 dependence in eqn (1), we address the experimental universal power-law relationship between the equilibrium degree of swelling $Q_{\text{eq}} = 1/\phi_{\text{eq}}$ in good solvent and the NMR-detected order parameter S_{eq} measured in swelling equilibrium, see Fig. 5a.

The theoretical treatment of S_{eq} is based on the insight that $S = \frac{3l^2 R^2}{5R_0^4} \propto f^2$, i.e., the order parameter is proportional to the square of the force $f = 3kT R/R_0^2$ that orients a given chain segment of length l into the direction of the end-to-end vector.²⁵ The experimental result, $S_{\text{eq}} \sim Q_{\text{eq}}^{-1.48}$, is in perfect agreement with a theoretical treatment for good solvents based on scaling theory, which embodies a careful consideration of the different scaling regimes of the structure of a network chain in semidilute solution.^{25,35} Note that the NMR-result being measured in swelling equilibrium implies that strong swelling inhomogeneities lead to a wide distribution in S_{eq} ,²⁹ requiring stable numerical procedures to extract a meaningful average value.²⁴ The given correlation was first observed by Cohen-Addad,³⁶ and ad-hoc taken as proof of the validity of de Gennes' c^* theorem,³⁷ which states that the equilibrium degree of swelling is equivalent to the overlap concentration of the corresponding solution of linear chains without the crosslinks.

The inset of Fig. 5a illustrates that the equilibrium degree of swelling corresponds to a semidilute state, where the chains inside the concentration blobs of size ξ exhibit excluded-volume statistics (expanded rather than Gaussian chains), while the string of blobs is in fact fully stretched. Edward's concentration blobs are thus equivalent to Pincus' force blobs^{37,38} at equilibrium swelling. As a consequence, segmental orientation fluctuations can only take place within a blob, and the swollen network is in fact equivalent to a c^* gel at the corresponding degree of swelling. Thus, NMR experiments on equilibrium-swollen networks provide a direct measure of blob size.

In this way, the c^* -model can be considered equivalent to the FR model, with one important difference: the elastic (entropic) contribution needs to be calculated on the basis of excluded-volume statistics, not the simple Gaussian statistics assumed in the affine and phantom models that are designed for the bulk state. This constitutes, in our view, the reason for the qualitative failure of the simple FR result commonly used to analyze swelling experiments in good solvents (notwithstanding the fact that reasonable results for M_c are usually obtained because the used χ parameter is based on an appropriate empirical "fudge").

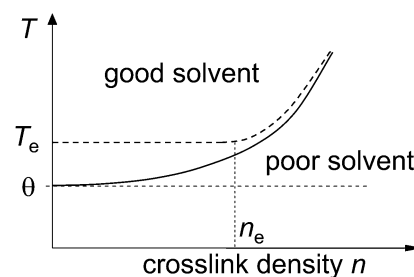


Fig. 6 "Network phase diagram," showing that the temperature region of Gaussian chain conformation (poor-solvent case) is enlarged in swollen networks. Entanglements, acting as physical crosslinks and limiting further the degree of swelling, prevent the observation of the transition between Gaussian and excluded-volume chains at the solution-state θ temperature even for very lowly crosslinked systems.

Now, addressing the θ and poor solvent regions, it is easily possible to derive another relationship between Q_{eq} and S based on FR theory, eqn (2), because simple Gaussian chain statistics is valid in this range.²⁶ The resulting S_{eq} features an explicit dependence on the excluded-volume parameter ν (thus χ), and is not a simple power law in Q_{eq} (only at $T = \theta$, $S_{\text{eq}} \sim Q_{\text{eq}}^{-2}$ for large Q_{eq}), yet experimental results can easily be fitted. The lines in Fig. 5b were obtained from a fit with only two free parameters, a spin-dynamics dependent constant A_0 that contains the unspecified proportionality factor in eqn (1), and the empirical parameter B from eqn (3) that determines ν . The joint fit to the whole range of poor to θ solvent data yields $B = 2.4$, in perfect agreement with the independently determined value from the thermodynamic data in Fig. 4a. As expected, the joint fit fails in the good-solvent region, which is why these data have been excluded (dotted lines).

We take these observations, using NMR as a novel probe of network thermodynamics, as another proof of the validity of FR theory for poor and θ solvents, provided that the elasticity contribution is described by the phantom model or related varieties that exhibit the same dependence on crosslink functionality. An in-depth discussion is given in ref. 26. We note that one must then use the full analytical form of the FR expression without any low-concentration approximations, as Q_{eq} is low and ϕ_{eq} correspondingly high. The necessary use of non-constant (crosslinking- or concentration-dependent) effective χ parameters should, however, not come as a surprise also in this region, as higher-order virial coefficients should contribute under these conditions, stressing the use of more elaborate equation-of-state theories rather than the simple Flory-Huggins treatment.

Finally, Fig. 6 depicts what we refer to as "network phase diagram," which explains why the θ point, i.e., the temperature below which a chain starts to exhibit Gaussian statistics, is not observable in a swollen network, but rather shifted to higher temperature. The plotted crossover relationship (solid line) is obtained again by simple scaling arguments,²⁶ and shows that the actual θ state is only realized in the limit of zero crosslink density. On top of that, real networks contain entanglements, and the fraction that is topologically trapped provides a constant contribution to n at swelling equilibrium. Thus, the

linear-solution θ point cannot be reached at all. These arguments might put the discussions about the apparent shift of the θ -temperature and the concentration (crosslink-density) dependence of χ for polymer networks swollen in good solvents into a different perspective. Instead of a sharp transition with a well defined limiting case of $T \rightarrow \theta$, a broad and smooth crossover between good and poor solvent regimes is expected. Being in the poor- or good-solvent regions in our phase diagram does or does not, respectively, imply the applicability of eqn (2) for the analysis of swelling results. The predicted behavior, in particular the effect of entanglements implies a favorably larger applicability range even for temperatures slightly above θ .

IV Conclusions

We have demonstrated that NMR experiments performed on swollen polymer networks provide an alternative test for theoretical models of network elasticity and swelling. On the one hand, high-resolution NMR methods in combination with Miller-Macosko theory can be used to obtain objective information on the crosslink density $n \sim 1/M_c$ and the functionality of crosslinks f , and this can be used as a gauge for network elasticity models. On the other hand, the most powerful, alternative NMR approach to characterize the network structure *via* its sensitivity to segmental orientation correlations, as quantified by the local, dynamic order parameter S , can be validated. It was shown that variations in f over a series of samples could be used to collect good evidence of the role of crosslink fluctuations and, within a single-chain description of rubber elasticity, rule out the affine network model in favor of the phantom model to describe the swollen state.

Based on our results employing the sensitivity of S to the thermodynamic state of a swollen network *via* its relationship to the network chain conformation, we could conclude that the popular Flory-Rehner theory of swelling is well applicable under conditions below or close to the θ state. For the good-solvent case the FR model is clearly and obviously stretched beyond its theoretical limitations, as can be inferred from the deviations of our NMR data from the predictions, and also from the direct observation of the equilibrium degrees of swelling as a function of temperature in this regime, which do not comply with the FR prediction. A proper treatment requires the consideration of excluded-volume effects on the chain statistics, for instance using scaling approaches and the blob concept. We finally repeat that a direct observation of the θ point in swelling of polymer networks is not easily possible, since finite length scales due to crosslinking and entanglements shift the apparent crossover between the good- and poor-solvent regimes to temperatures above θ .

In our other contribution in this issue,³¹ we extend our studies to partially swollen networks below equilibrium. We will specifically focus on additional contributions to network elasticity in the dry state, one consequence of which is highlighted in Fig. 1b on the example of largely different apparent defect contents of dry and swollen networks.

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