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Segmental Order Parameters and Swelling in Polymer Networks

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Summary: We study segmental order parameters in polymer networks in good solvent. In particular we consider the tensor order parameter which characterizes the degree of orientational order of segments and which is directly related to the residual coupling constant obtained in NMR-experiments. Using a simple relation between the order parameter and the force acting on the chain end at a given extension we derive an universal relation for the order parameter for concentrations above the overlap threshold. Considering polymer gels at the equilibrium state of swelling we predict a unique relation between the tensor order parameter and the correlation length (blob size) of the gel. Experiments applying multi-quantum NMR-methods to both end-linked and randomly cross-linked polymer networks are in excellent agreement with this prediction. We critically discuss the widely used Flory-Rehner model of network swelling and show that initial decay of the tensor order parameter as observed in experiments at low degrees of swelling can be explained as a solvent effect without making additional assumptions about constraint release processes during swelling.

Keywords: elastomers; NMR; polymer networks; residual dipolar couplings; segmental order parameter

Segmental Order in Polymer Networks

Polymer networks are disordered solids. To differentiate between a polymer network and a polymer melt on the basis of statistical mechanics one has to introduces order parameters which reflect local persistent order and which are not trivially related to a macroscopic degree of order. Here, we discuss such order parameters characterizing the orientational properties of chain segments. These results, on the other hand, can be directly related to a certain class of NMR-experiments, in particular to the so-called residual dipolar coupling constant (RDC).[1–4]

Figure 1 illustrates the problem to define a macroscopic orientational order parameter in a disordered system such as a polymer network. Individual network strands display a residual orientation $<\vec{b}_k>$ of a segment k within the chain. Here, $\vec{b}_k$ denotes the unit vector of the orientation of the segment k and $<...>$ denotes the thermal average (or time average) over all conformations of the polymer. However, the average over all segments in the sample $[<\vec{b}>]$ is zero because chain orientations between cross-links are randomly distributed. Here [...] denotes the sample average over all segments. A similar problem arrises in spin-glasses, where spins are locally oriented but due to random exchange interactions there is no macroscopic magnetization, see.[5] There are two possibilities to define a macroscopic order parameter which

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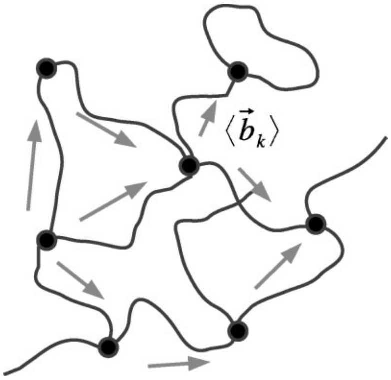

Figure 1.
Sketch of a part of a network structure. The segment orientation of a given strand is restricted by cross-links the resulting orientation vectors are indicated as arrows. Since the chain orientations are random in the sample there is no global orientation vector.

circumvents this problem. First, one can consider the expression

$$m = [< \vec{b} >^2], \tag{1}$$

where the squares of the residual orientation vectors are summed up, and which yields a finite value if local order exists. We denote this quantity as the *vector order parameter* since it is based on the vector of the segment orientation. Although theoretically very usefull, this definition has two disadvantages. First, it relies on the vector-like orientation of segments which does not correspond to the fact that usually the orientational properties of segments are mirror-invariant (it does not matter from which end of the chain segments are counted). Second, it is difficult to find an experimental method to measure the vector order parameter. Therefore, we introduce an alternative definition based on the orientation tensor of a segment given by:

$$S_{\alpha\beta} =< b_\alpha b_\beta > -\frac{1}{3}\delta_{\alpha\beta}, \tag{2}$$

where the Greek indices denote the Cartesian components of the orientation vector and $\delta_{\alpha\beta}$ is Kronecker's delta. Obviousely, this expression is invariant with respect to an inversion of the (arbitrary chosen) vector orientation. Also, the trace of the matrix S is strictly zero. A corresponding macroscopic invariant can be defined as

$$s = \left[\sqrt{\frac{3}{2} TrS^2}\right]. \tag{3}$$

Here, TrS^2 denotes the trace of the squared matrix S given in Eq. (2). We will call this parameter the *tensor order parameter* since it measures the strength of tensorial orientation. It can now be shown, that this parameter is directly related to the RDC which can be measured by NMR.[6]

In the following, we consider the case where the segment orientation is uniaxial with a given direction which is the end-to-end vector of the strand fixed by the cross-links, see Fig. 2. Then, the tensor order paramerter can be obtained from the the second Legendre polynomial of the segment orientation with respect to the end-to-end vector $\vec{R}$. If we denote the angle between $\vec{R}$ and a given segment of length l ($\vec{l} = l\vec{b}$) by θ, we obtain

$$s = \frac{1}{2}\left[(3 < \cos^2(\theta) > -1)\right]. \tag{4}$$

A Gaussian chain at fixed end-to-end distance yields

$$s = \frac{3}{5}\left(\frac{R^2}{N^2 l^2}\right) = \frac{1}{15}\beta_G^2, \tag{5}$$

where l and N denote the length of a statistical segment and the number of such

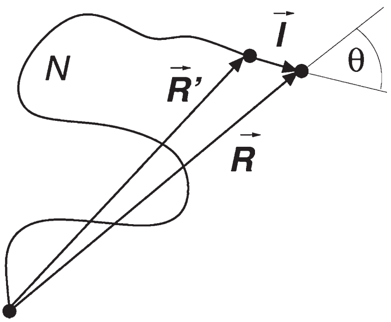

Figure 2.
Sketch of a chain conformation with a tagged segment at the end.

segments in a chain, respectively. This results in the well known relation $[s] = \frac{3}{5}\frac{1}{N}$, where the sample average over R^2 yields Nl^2 in an undeformed polymer network. It is worth noting that the parameter

$$\beta_G = \frac{3R}{Nl} = \frac{3Rl}{R_0^2} \tag{6}$$

corresponds to the *force* (in units of kT/l) which acts on the segment at the end of the chain (which is the same for all segments in case of ideal chains) by the fixing the chain at the end-to-end distance R, see Fig. 2. In the above Equation we have used the free end-to-end distance $R_0^2 = l^2N$.

This idea can be directly extended to a chain in a semi-dilute solution. Since we are going to discuss polymer networks in the swollen state, we characterize the state of dilution by the volume swelling ratio

$$Q = V/V_0, \tag{7}$$

where V and V_0 are the volume of the network after and before swelling, respectively. The volume swelling ratio is the inverse of the segment concentration related to the melt state as unity denoted by $c = 1/Q$. In the semi-dilute state, the overall chain conformation displays Gaussian behavior, but locally excluded volume effects determine the conformation. This can be best visualized using the blob-concept as introduced by Daoud and de Gennes, see,[7] which we have sketched in Fig. 3. The extension of the free chain is given by

$$R_0^2 \sim (N/g)\xi^2 \sim NQ^{(2\nu-1)/(3\nu-1)} \sim NQ^{1/4}. \tag{8}$$

Here, we have used the relation $\xi \sim g^\nu$ for the blobs where ν denotes the Flory exponent. In the last relation we have used Flory's value of $\nu_F = 3/5$.

Using the argument that the parameter β which determines the strength of the orientation is given by the force acting on the segment at the end of the chain, we obtain using Eq. (8)

$$\beta_{SD} = \frac{3Rl}{R_0^2} \sim \frac{R}{lN} Q^{-1/4}. \tag{9}$$

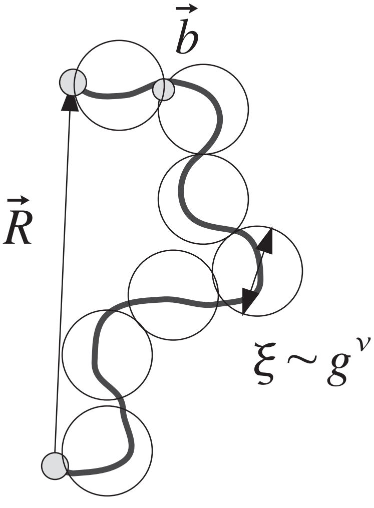

Figure 3.
Sketch of a chain conformation in a semi-dilute state. The chain can be considered as an ideal chain of blobs. Within the blobs of size ξ the chain displays good solvent statistics.

For the case of a single chain in good solvent we obtain using the same argument[8]

$$\beta_D \sim \left(\frac{R}{Nl}\right)^{\nu/(1-\nu)} \tag{10}$$

All these results can be obtained analytically by considering the distribution function of the chain in various states of dilution, and by focussing on the last segment as sketched in Fig. 2. For the dilute solution the so-called Fisher distribution has to be used.[7,9,10] Moreover, in this case it has to be shown that the behavior of the end segment is characterstic for the overall chain.[10]

It is worth noting that Eqs. (9) and (10) coincide at c^* where the chains just overlap and $R \sim lN^\nu$. On the other hand, Eq. (6) is a limiting case of Eq. (9) for $Q = 1$. Therefore, we can write down a *universal relation* for the tensor order parameter valid for all degrees of swelling relevant for a polymer network between $Q = 1$ and $Q = 1/c^*$:

$$s \sim \frac{R^2}{R_0^4}, \tag{11}$$

where R_0 denotes the reference state at the given degree of swelling. This relation should replace Eq. (5) which has been frequently applied to analyze NMR data of dry and swollen polymer networks.[11–14] In the following, we will discuss the consequences of these results for polymer networks in the swollen state.

Polymer Network at Swelling Equilibrium

Polymer networks can take up large amounts of solvent, thus considerably diluting the polymer fraction. The simplest model is to consider a deformation of individual network chains where end-points are fixed and are displaced affinely with the macroscopic deformation.[15] This model has been extended to investigate the swelling behavior of polymer networks by Flory and Rehner.[16] Here, the end-to-end distance follows directly the macroscopic deformation: $R = lN^{1/2}Q^{1/3}$. In all stages of swelling the network is in a semi-dilute state. In fact, it can be shown that the Flory-Rehner results can be derived by assuming that chains are not allowed to desintersperse.[17] Using Eqs. (8) and (11), we obtain

$$s_{FR} \sim \frac{1}{N} Q^{2(2-3\nu)/(3\nu-1)} \sim \frac{1}{N} Q^{1/6}. \qquad (12)$$

Swelling equilibrium, $\overline{Q}$, is obtained when the osmotic pressure of the network is equal to the negative elastic pressure exerted by the chains due to affine stretching. Using scaling arguments for the osmotic pressure and for the elastic free energy in the semi-dilute state, following Obukhov, Colby and Rubinstein,[18] one can generalize the original result by Flory and Rehner for the swelling equilibrium: $\overline{Q}_{FR} \sim N^{3(3\nu-1)/4}$ ($\overline{Q}_{FR} \sim N^{3/5}$ for ν_F). Using the result of Eq. (12) for the swelling equilibrium we obtain

$$\bar{s} \sim \overline{Q}^{-2\nu/(3\nu-1)} \sim \overline{Q}^{-3/2}, \qquad (13)$$

using ν_F for the last relation.

For c^*-gels the equilibrium degree of swelling, $\overline{Q}$ corresponds to the overlap condition of the network strands given by $\overline{Q} = Q^* \sim N^{3\nu-1}$. Using Eq. (11) with $R = R_0 \sim N^{\nu}$, we obtain $\bar{s} \sim N^{-2\nu}$ which can be expressed in terms of the equilibrium swelling ratio as

$$\bar{s} \sim Q^{*\,-2\nu/(3\nu-1)}. \qquad (14)$$

Interestingly, both models yield the *same* relation between segmental order parameter and degree of swelling under good solvent conditions regardless of the fact that both models predict very different properties of the gel at equilibrium: While for the c^*-model network chains just overlap and are not stretched with respect to their solvent state, in the FR-model network chains are under semi-dilute conditions and highly stretched due to the affine deformation.

In Fig. 4 we display experimental data for very different systems: natural rubber and PDMS networks, both end-linked and randomly cross-linked in bulk and in solution. Very good agreement between the theoretical prediction given by Eqs. (14) and (13) is obtained, and is in marked contrast to Gaussian statistics. The best fit to the data is obtained with a slope of -1.48. We like to add that the experimental findings are in excellent agreement with results of computer simulations using the bond fluctuation method presented in Ref. [10].

It is important to note that the predictions made in Eqs. (14) and (13) do not depend on the nature of the constraints at swelling equilibrium. Beside cross-links, also entanglements[17] might determine the equilibrium degree of swelling. This does not matter for the result of both Equations because only directly measureable quantities (s and Q) are related, and the strand length (which can be either chain parts between cross-links or between entanglements) enters only implicitly.

Discussion and Conclusion

In order to understand the conincidence of both models with respect to the tensor order parameter, we can rewrite Eqs. (14)

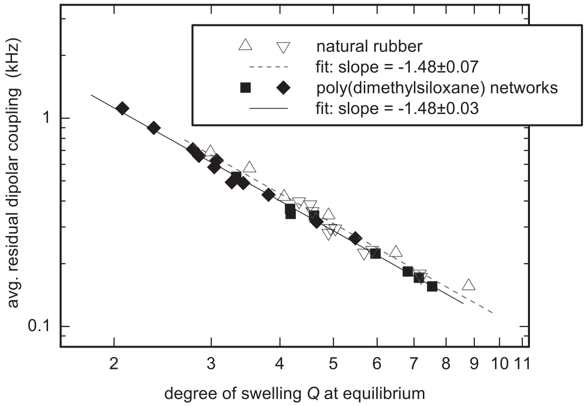

Figure 4.
Average RDCs at swelling equilibrium vs the equilibrium degree of swelling in toluene (log-log plot) for different PDMS and natural rubber (NR) networks. The PDMS series includes networks that were synthesized at lower polymer volume fractions, down to $\phi_{\text{pol}} = 0.25$.

and (13) in the following form

$$\overline{s} \sim 1/\xi^2, \qquad (15)$$

where $\xi \sim Q^{\nu/(3\nu-1)}$ denotes again the correlation length of a semi-dilute solution, see Fig. 3. Thus, *the tensor order parameter measures the blob-size* of the gel swollen at equilibrium. A close look at the Flory-Rehner model reveals the reason for this unexpected result. The mixing free energy is of order kT per segment while the elastic free energy is of order kT per chain only. Thus, elasticity is not an important contribution at the early stages of swelling. Due to the affine deformation of the network chains *a priori* assumed in the Flory-Rehner model, the swelling process stops only if the stretchability of the chains is reached. In the equilibrium state the chains form stretched strings of blobs of size ξ as illustrated in Fig. 5. The chains' extension is given by

$$\overline{R} \sim (N/g)\xi \sim \overline{Q}^{(3\nu+1)/3(3\nu-1)} \sim N^{(3\nu+1)/4} \qquad (16)$$

The last relation leads to the well known result of the FR-model by using Flory's value of the ν-exponent: $\overline{R} \sim N^{7/10}$. In this extended state, *no* orientation fluctuations occur on length scales larger than the blob size. The strong stretching force effectively fixes the concentration blobs as if they where crosslinked. Thus, the order parameter corresponds to that of a c^*-gel at the corresponding swelling ratio. We note that this state of the polymer network is unstable with respect to any rearrangements of network strands. Desinterspersion both decreases the stress on the individual network strands and increases the degree of swelling (increasing the mixing free energy).

Is it possible to discriminate between both models? In order to do this, network swelling has to be observed at intermediate stages of swelling below swelling equilibrium. For the Flory-Rehner theory, Eq. (12) is valid and predicts a monotonous increase of the order parameter with Q. We

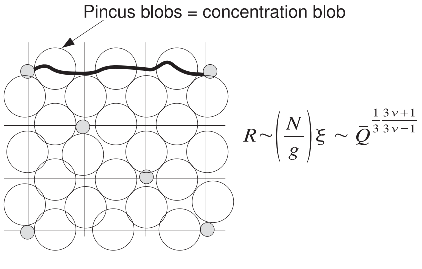

Figure 5.
Flory-Rehner model: At swelling equilibrium network strands are overstretched and form a string of blobs (open circles) between crosslinks. Fluctuations are restricted to the correlation length ξ.

note that the power of 1/6 is much weaker than the result of the Gaussian theory where an exponent of 2/3 is predicted. However, experimental results often display a constant or non-monotonous behavior of the tensor order parameter (RDC) at low degrees of swelling and a much stronger increase at high degrees of swelling.[19–21] An example from our own work is given in Fig. 6.

Clearly the Flory-Rehner affine network model cannot explain such findings. It is worth noting that non-affine deformation and rearrangement of large connected parts (clusters) of the network structure has been reported in computer simulations[23] and has been discussed in the experimental literature since a long time, see.[24] Using Eqs. (11) and (8) one can easily show that sub-affine deformation which is below a scaling relation of $R \sim Q^{1/4}$ leads a decrease of the tensor order parameter. If the network strands desintersperse and behave according to the semi-dilute state, $R \sim Q^{1/8}$, even a decrease of the order parameter is obtained. Thus, in the early stage of swelling ($Q < 2$) the affine assumption fails. It is worth noting that the so-called swelling anomaly observed for difference osmotic pressure of a polymer network and the corresponding polymer solution falls in the same range of intermediate degrees of swelling.[25] Also these observations can be explained using a non-affine deformation model of the polymer network.[26]

The rather strong increase of the tensor order parameter at later stages of swelling might be attributed to constraints due to trapped entanglements which become localized during swelling[6] and eventually contribute to the equilibrium state of the gel.[17] To understand the effect of trapped entanglements, however, further studies are necessary.

To conclude, we have shown that solvent effects (chain statistics) change the residual dipole coupling measured in NMR experiments. This is because the theoretically accessible tensor order parameter depends on the fluctuation statistics of the chain and not only on the geometrical constraints. Using these results, we have shown that the tensor order parameter at swelling equilibrium is directly related to the correlation length independent of the theoretical model used. The behavior of the tensor

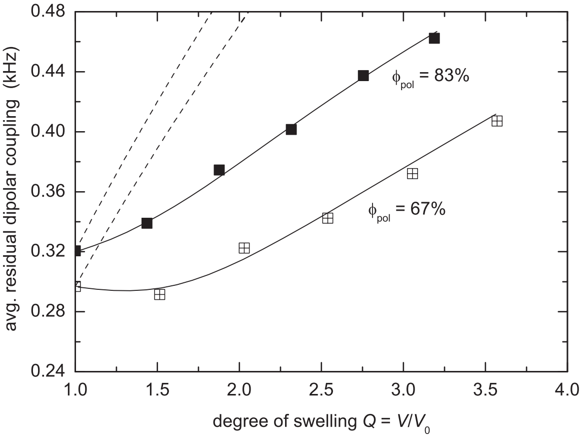

Figure 6.
Experimental results for the averaged RDC $\sim s$ as a function of Q for two end-linked polydimethylsiloxane networks (linear precursor $M_n = 5200$ g/mol), crosslinked in the presence of toluene at different polymer volume fractions ϕ_{pol}, swollen in good solvent (toluene) and θ solvent (styrene at 35 °C [22]); see ref. [21] for details. Solid lines just guide the eye, and dashed lines are the affine predictions. Generally, the RDC is lower for good solvent conditions at the same degree of swelling. The arrows indicate the reduction of the equilibrium degree of swelling in θ solvent.

order parameter at low degrees of swelling indicate a non-affine deformation behavior of the network strands in this range.

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