

030507 Quiz 10 Polymer Properties

- 1) Lorthioir et al. describe the importance of determining the sign of the orientational order parameter. Their first paragraph is repeated below. (Lorthioir, C. Deloche, B., Courtieu, J. *Macromolecules* 2001 34 8835-8837).

Introduction. Uniaxial fluids such as liquid crystals, liquid crystal polymers, polymers under constraint, etc., have been widely studied using NMR. Indeed, this approach is very sensitive to the symmetry of molecular motions and gives access to the so-called orientational order parameter S , which describes the anisotropy of collective fluctuations around the uniaxial symmetry axis of the system. Such NMR investigations are very useful in liquid crystals for characterizing the breaking of symmetry at phase transitions¹ as well as in polymers in regard to the viscoelastic or elastic properties.² However, the question of the sign of S is rarely evoked and difficult to solve experimentally. The sign of S is determined by the direction of molecular fluctuations relative to the symmetry axis, which allows one to deduce the average orientation and conformation of the molecules. Such data are then relevant in the study of the macroscopic properties of the considered materials. Obviously, the question of the S sign is meaningless when the degree of order is high ($|S| > 0.5$) as in a nematic mesophase, S being inherently positive. On the other hand, the question remains opened and relevant for systems of low order ($|S| < 10^{-2}$) such as molten polymers under constraint. Experimentally, a direct and unambiguous determination of the sign of S from a single NMR spectrum would be very useful.

- Define uniaxial symmetry axis of the system for a rubber sample that is compressed.
- What would be the difference between a system that displayed $S = 0.3$ and $S = -0.3$?
- Why is the sign question meaningless if $|S| > 0.5$.
- Lorthioir et al. define S as $\overline{P_2(\cos \theta)}$, the average of the second order Legendre polynomial. Give a simpler definition of the orientational order parameter from class and define the terms.
- The following figure shows Lorthioir et al.'s results for a PDMS network under deformation. Why is the data not plotted versus the extension ratio, λ ?

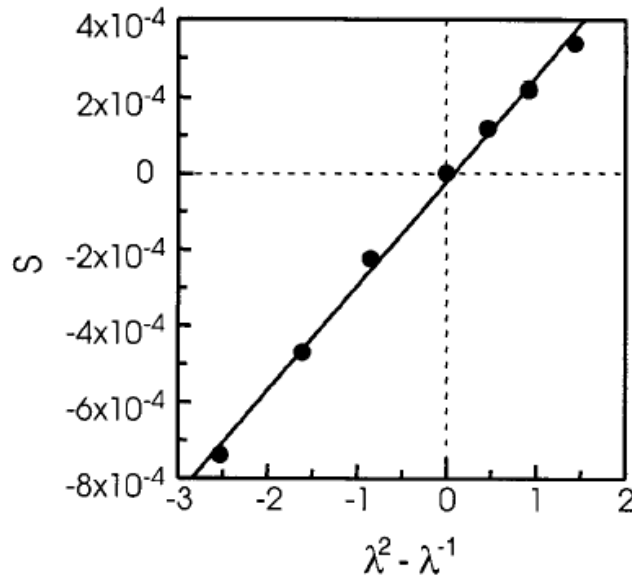


Figure 4. Order parameter S (obtained from ^{13}C NMR measurements) vs the strain function $\lambda^2 - \lambda^{-1}$, the deformation ratio λ varying between 0.38 and 1.46. The solid line represents the linear fit of the data.

- f) In class we used a symmetric function $\langle f \rangle = \langle f^2 \rangle$ to calculate the anisotropy of polarizability for a Rouse spring, $\chi_{spr} = n_m \langle f \rangle$, where $\langle f \rangle$ is related to the orientational order parameter. How does Lorthioir et al's plot support this symmetric function?
- g) Describe a simple measurement for the determination of the orientational order parameter or $\langle f \rangle$. (Give an experimental sketch and some equations.)
- 2) In class we developed an equation for rubber elasticity by two approaches, using the extension ratio and using the Finger tensor, \underline{B} .
- Give three reasons you need to use the Finger tensor approach to describe a stress energy function for a strained rubber.
 - Define the Finger tensor.
 - Give the equation of state for an ideal rubber in terms of the Finger tensor.
 - Calculate the Finger tensor for simple shear strain.
 - Use this tensor and the equation of state of part c) to calculate the relationship between the shear stress and the strain.
 - Use this tensor to calculate the first normal stress difference for a sheared rubber, $(\sigma_{xx} - \sigma_{yy})$.
 - If you were planning a dynamic mechanical measurement on a polymer sample would you prefer to run the instrument in tension or in shear? Why?
 - In polymer flow the first normal stress difference leads to unexpected flow behavior such as swelling of polymer streams normal to the flow direction. Is this behavior due to a special feature of long chain molecules or might it be seen in other systems? Explain.

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1a) The symmetry axis is the draw or compression direction. For a LC polymer it is the direction of the electric, magnetic or shear field.

b) The difference is that the positive orientation indicates orientation in the direction of the symmetry axis and the negative indicates orientation normal to this axis.

c) For a perfectly ordered system S is 1 for a random system S is 0, for a system that perfectly orients normal to the symmetry axis S is -0.5 so negative orientation values below -0.5 are not possible by definition.

d)
$$\frac{3\langle \cos^2 \rangle - 1}{2}$$

e) This plot is similar to a Mooney-Rivlin Plot. The x-axis is the native axis for tensile rubber elasticity when considering pure strain.

f) When his x-axis is 0 the deformation changes from compression to tension. Then he shows that there is symmetry in orientation about 0 and the response function should be symmetric.

g) This is the birefringence measurement described in class. Some detail is needed in this answer.

2 a) I) Tensor is needed for high elongations II) Tensor is needed to remove consideration of translational and rotational deformation III) Tensor is needed to describe arbitrary deformation and response such as normal stress response in shear.

b)
$$B_{ij} = \frac{r_i}{r'_k} \frac{r_j}{r'_k}$$
 where the primed terms are the undeformed state.

c)
$$\underline{\underline{=}} = G\underline{\underline{B}} - P\underline{\underline{1}}$$

d) See the notes

e) Same

f) Same

g) Shear since the stress and strain are proportional from rubber elasticity while a complicated relationship exists for tension.

h) The feature is due to the equation of state for a rubber given in part c). This relies only on a connected structure that is incompressible. It is not inherently related to the molecular structure of a polymer.