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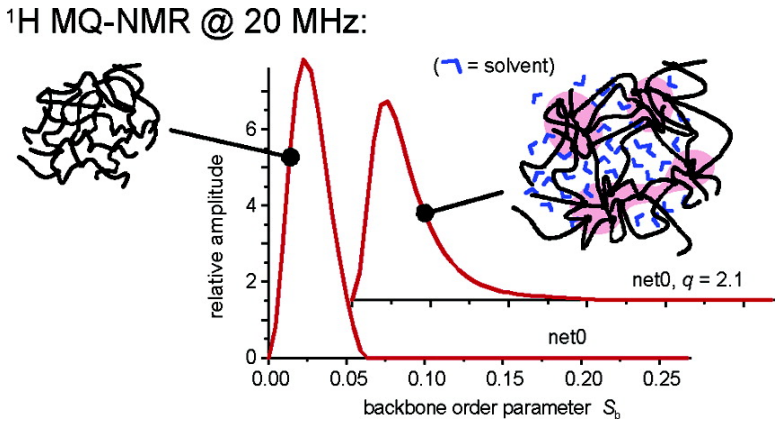


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# Detection of Heterogeneities in Dry and Swollen Polymer Networks by Proton Low-Field NMR Spectroscopy

Kay Saalwächter*

*Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Strasse 31, D-79104 Freiburg, Germany*

Received September 2, 2003; E-mail: kays@makro.uni-freiburg.de

Solid-state NMR is able to provide a fascinating wealth of information on structure and dynamics in industrial products such as polymers and elastomers.[1] Recently, we have introduced a robust strategy based on proton multiple-quantum (MQ) spectroscopy, by which issues as complex as molecular-scale motional heterogeneity in single-component elastomer systems can be addressed quantitatively.[2] While the assessment of such information holds promise for very specific product screening applications, the investments in high-field instrumentation and skilled personnel may be prohibitively high. Cost efficiency, simple sample preparation, as well as robust and automated experiments are among the primary requirements in quality control. Therefore, easy-to-use low-field proton-only NMR analyzers, with Larmor frequencies of usually less than 30 MHz, have gained importance in many industrial applications,[3] but also for some high-level investigations such as interfacial phenomena in polymeric systems.[4] Our aim at the outset was, therefore, to evaluate in how far advanced MQ spectroscopy can be performed on low-field instrumentation, while retaining fully quantitative information.

Usually, proton low-field NMR applications are based on simple time-domain relaxation experiments and calibration of the instrument response or model-dependent analyses of the relaxation functions. Yet, for good reproducibility, the magnetic field as well as the rf pulses must be sufficiently stable. E.g., the minispec mq20 manufactured by Bruker, provides proton line widths of less than 1 kHz, rf nutation frequencies exceeding 100 kHz, reliable phase cycling, and data sampling on the sub-$\mu$s time scale, making such an instrument well adapted for advanced solid-state applications such as MQ spectroscopy. These methods are among the most recent and versatile experiments which provide information on local chain order in polymers.[5] Our work in this area was concerned with the extension of this methodology to the determination of chain order *distributions*, i.e., molecular-scale heterogeneity, in network samples, which becomes possible when suitable pulse sequences[6] and a reliable normalization approach are used.[2]

We here show for the first time that not only can such up-to-date MQ NMR techniques be implemented on a low-field instrument, but that the results are also virtually identical to those obtained at high field. While the investigation of cross-link density[7] and the application of simple MQ pulse sequences[8] is in fact possible even in the highly inhomogeneous field of NMR surface probes, our approach is distinguished from these and other reported applications of MQ NMR in that it requires no calibration and is very robust toward slow dynamics in the sample and experimental imperfections.[2] We highlight the potential of our method by measurements on a swollen system, where the existence of heterogeneities is a subject of ongoing discussion.[9]

The response of polymeric networks or melts in proton NMR experiments is commonly analyzed in terms of residual dipolar interactions.[10] These originate from imperfect motional averaging of chain segments fluctuating rapidly between topological constraints such as cross-links or chain entanglements, and may reach a magnitude of several percent of the corresponding static interaction. Residual interactions are directly proportional to a dynamic order parameter of the polymer backbone,

$$S_b = \frac{D_{res}}{D_{stat}} \frac{1}{P_2(\cos \bar{\alpha})} = \frac{3}{5} \frac{r^2}{N} \qquad (1)$$

and can be calculated from the residual dipolar coupling constant, $D_{res}$, by comparison with its static counterpart, $D_{stat}$. $\bar{\alpha}$ is the average orientation of the internuclar coupling vector with respect to the segmental orientation. As indicated by the RHS of eq 1, $S_b$ is related to $r$, the normalized deviation of the end-to-end vector from its average, unperturbed melt state, and to $N$, the number of statistical chain segments between the constraints.[11] Therefore, the measurement of $D_{res}$ provides information on the cross-link density,[12] is directly related to the mechanical properties of the sample, and may further be used to test predictions of network theory.

The $^1$H MQ experiment used herein embodies the application of a specific double-quantum (DQ) excitation pulse sequence of variable duration $\tau_{DQ}$,[6] along with a phase cycle, by which a DQ-filtered and a reference intensity can be measured. The sum of these two contributions comprises the full magnetization of the sample subject to relaxation and decay due to experimental imperfections, and is used to normalize the DQ-filtered intensity. The resulting DQ build-up curve can then be analyzed with a monomer-specific build-up function,[2]

$$I_{nDQ} = 0.5\,(\,1 - \exp\{\,-31.91(D_{res}/2\pi)^2\,\tau_{DQ}{}^2\,\}\,) \qquad (2)$$

here given for poly(dimethylsiloxane) (PDMS). $D_{res}/2\pi$ and $\tau_{DQ}$ are in kHz and ms, respectively. Details on the experimental procedure and an in-depth discussion of the limits of the method may be taken from ref 2.

Experiments were carried out on PDMS model networks prepared by end-linking of precursor polymers with average molecular weights of 40 700 and 780 g/mol. We have here re- investigated mono- as well as bimodal networks, where for the latter, mixtures of short and long chains were cross-linked. Apart from the pure long-chain network (net0), experimental data for two mixtures containing 30% and 70% w/w short chains (net30 and net70, respectively), obtained on a Bruker mq20 minispec (90° pulses of 2.1 $\mu$s length), are compared in Figure 1a and b with previously published results obtained at high field.[2] Similar amounts of sample (about 100 mg) as well as the same number of transients (64) were used. The build-up functions, as well as the corresponding order parameter distributions, are reproduced quantitatively. They indicate a linear mixing law of short- and long-chain contributions,[2] and thus reflect microscopic heterogeneity. The deviations, notably the loss of the very small, yet reproducible, contribution of more ordered chains detectable for net0 at high field, are mainly due to a larger


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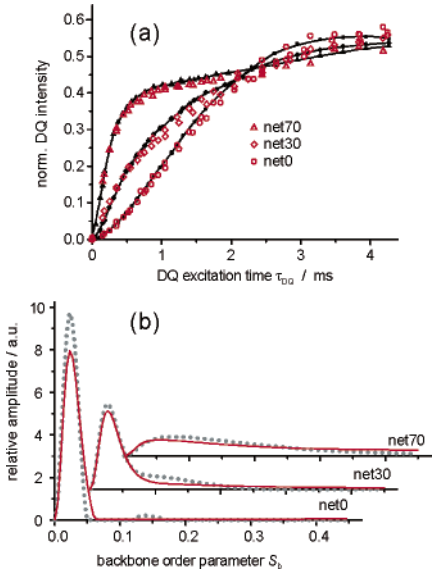


***Figure 1.*** (a) DQ build-up curves for net0, net30, and net70, acquired at 20 MHz (open symbols), as compared with data obtained at high field (500 MHz, solid lines and symbols). (b) Corresponding order parameter distributions (solid lines) as obtained by analysis of the responses in (a) using eq 2 and fast Tikhonov regularization,[2,13] again compared with high-field results (dotted lines).

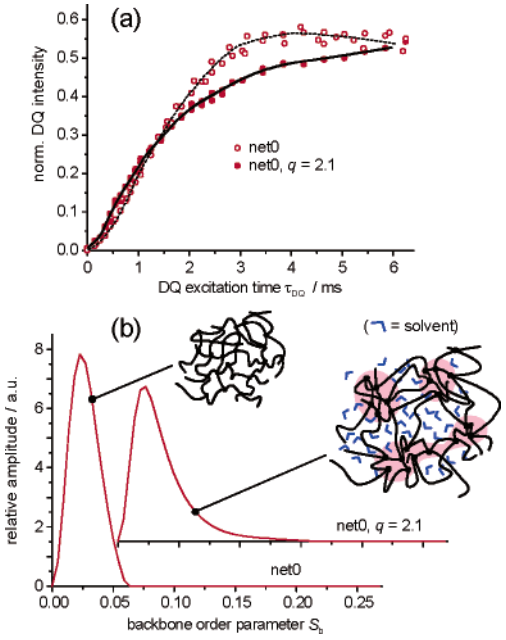


***Figure 2.*** (a) DQ build-up curves for a monomodal long-chain network sample, dry (open circles) and carefully swollen in octane vapor (solid circles), acquired at 20 MHz. The degree of swelling, $q$, is given in terms of the weight ratio $M_{swollen}/M_{dry}$. The lines are guides to the eye. (b) Corresponding chain order parameter distributions, indicating significant swelling heterogeneity.

scatter of the minispec data, arising from the relatively small sample size. Five to ten times more sample could easily be fitted into the central part of the probe, where the rf homogeneity is still acceptable. Under these conditions, experimental noise would represent a negligible source of error.

The large potential of the method is demonstrated by the comparison of dry and moderately swollen net0. Note that the long-time exponential tail of the reference intensity associated with the swelling agent in the latter sample needs to be subtracted before normalization. From the data given in Figure 2, it is apparent that the chain order distribution becomes broader, while the average chain order parameter is only slightly increased. The classic, affine theory of network swelling[14] would suggest a more pronounced increase in $S_b$ and no change in the distribution. Anomalies concerning the average NMR-detected chain order parameter have been observed and explained before.[15] However, potential heterogeneities have as yet eluded NMR analysis, but are expected in light of more recent theoretical approaches.[16] It is predicted that topologically frozen inhomogeneities should be present already in the dry state and become visible upon swelling. Until now, only advanced light, X-ray, or neutron scattering experiments were used to investigate these controversial issues.[9] A more detailed NMR study of these phenomena is currently underway in our laboratory.

In summary, we believe that the $^1$H MQ NMR methodology will continue to provide unique insights into heterogeneities in molecular structure and dynamics of polymers and elastomers. Heterogeneities in polymer gels can be expected to have a significant influence when, e.g., separation membrane or proton conductor applications in fuel cells are considered. The advantages of user-friendly low-field NMR analyzers in terms of simple sample handling, automatic calibration, and automated MQ-spectroscopic data acquisition and analysis, is envisaged to stimulate the development of more quantitative and specific product screening approaches for the polymer industry.

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