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Summary of the PhD student Radu Fechete work

In the last two years Radu Fechete was working in my group as a PhD student. He obtained many interesting results related to the characterization of elastomers and biopolymers by advanced NMR methods and *in situ* detection of oil by mobile NMR sensors. A short presentation of these results is given below:

1. *Chain orientation and slow chain dynamics by advanced NMR methods*

An important objective of polymer science is to establish relationships between the microscopic structure or molecular dynamics and the macroscopic properties of materials. Once established, this knowledge contributes towards to the design of polymers with improved properties. Thus, a key aim of polymer science is the acquisition of information on structure, morphology, and chain dynamics on the microscopic, mesoscopic and macroscopic scale by employing NMR spectroscopy and imaging. The unique chemical selectivity and high flexibility of these techniques allow one to study structure, chain conformation and molecular dynamics in considerable detail and depth.

1.1. A novel NMR method based on the decays of the mixed ^{1}H echo represented by a combination of the magic and the Hahn echoes was applied in a series of cross-linked elastomers. The mixed echo refocuses the homogeneous and inhomogeneous spin interactions. It allows the investigation of the fluctuation of the dipolar interaction of polymer chains in the slow motion regime. The method accounts for multispin dipolar interactions and eliminates the interference of linear spin interactions due to chemical shielding, magnetic field inhomogeneities, local susceptibility variations, and heteronuclear dipolar interactions. For the first time the multispin dipolar correlation functions characterizing the mixed echo decay are derived in the approximation of a single correlation time and for a distribution of correlation times. Based on these dipolar correlation functions the ^{1}H residual second van Vleck moment, correlation times and parameters of the correlation time distribution are determined for a series of natural rubber samples with different cross-link densities. The segmental order measured by the residual second van Vleck moment was shown to scale with a polynomial dependence on cross-link density or shear modulus. This can be interpreted by considering high-order corrections to a Gaussian distribution of the end-to-end vectors. By assuming a log-Gaussian distribution function for the correlation times and the validity of the Williams-Landel-Ferry (WLF) equation, the center of gravity and the logarithmic width of the distribution function of the correlation times describing the slow motion of the network chains

scale with the degree of topological constraints and the chemical cross-link density by a power-law with exponents 2.85 ± 0.65 and 3.09 ± 0.23, respectively.

The results have been published in J. Chemical Physics [7].

1.2. An original NMR method was also proposed for measuring only the segmental chain orientation for elastomers which can be also applied to any soft solids. This method is model free and it allows filtering only the solid-state behavior of polymer chains in elastomers. The correlation between the ^{1}H residual van Vleck moments and the shear modulus of a series of cross-linked natural rubber samples was established.

The results will be submitted to Chemical Physics Letters [12].

1.3. The possibility to enhanced the sensitivity of some NMR parameters to the cross-link density by detection of ^{1}H high-order multiple-quantum coherences in elastomers was recently demonstrated. This method can be applied to characterize many soft solids and to establish correlation with their viscoelastic properties.

A manuscript is in preparation on this topic [16].

2. *Segmental anisotropy in strained elastomers by ^{1}H NMR of multipolar spin states*

A well-known consequence of the theory of rubber elasticity is bond orientation. Deformation of an elastomer induces anisotropy of the backbone bonds of the polymer coil. In recent NMR studies of rubber elasticity the mechanism of deformation and the orientation of network chains has received increasing attention. One and two-dimensional NMR spectroscopy of ^{2}H and ^{1}H has been used intensively in the last decade to measure the dipolar correlation effect, homonuclear and heteronuclear residual dipolar couplings, and corresponding dynamic order parameters.

2.1. The local segmental anisotropy induced by a uniaxial applied force in elastomers is investigated by NMR in terms of ^{1}H dipolar encoded longitudinal magnetization decays and double-quantum coherences build-up curves. These multipolar nuclear spin states were measured as a function of the angle θ between the static magnetic field and the direction of the applied force. The experimentally determined angular dependence of the effective residual dipolar couplings shows a minimum around the magic angle. These NMR methods offer the possibility to investigate in great detail the mechanisms responsible for the induced local anisotropy in strained polymer networks.

Results of this work were published in Macromolecules [4].

2.2. Another NMR technique based on the dipolar correlation function which allows to measure residual second van Vleck moments and distribution of correlation times was used to investigate the effect of uniaxial deformation and orientation in cross-linked elastomers.

A paper is in preparation and we intend to submit it in Macromolecules [15].

2.3. Single-side NMR is particularly suitable for the measurements of the segmental anisotropy induced in elastomers by uniaxial forces or local strain. Proton transverse nuclear magnetic relaxation was investigated with the NMR-MOUSE® by the Hahn-echo decay in cross-linked natural rubber bands to measure the dependence on the angle between the direction of the uniaxial stretching force and the $\hat{Z}$ axis defined perpendicular to the magnet pole faces of the NMR-scanner. The anisotropy effect on the Hahn-echo decay is correlated with the extension ratio, and it is more evident in the liquid-like regime of the decay. A weaker encoding of the segmental anisotropy is detected by ^{1}H multi-pulse sequences. An understanding of the angular dependence is obtained by an analytical theory of the Hahn-echo decay adapted to the case of stretched elastomers and strongly inhomogeneous magnetic fields. The spin system response based on solid-like as well as liquid-like contributions for a spin-½ pair attached to chain segments in a network was considered. Two distinct mechanisms responsible for the anisotropy induced by the uniaxial stretching force were taken into account. The dynamic order parameter and the effective inter-chain interaction constant were estimated from ^{1}H residual second van Vleck moments. Using these parameters the segmental anisotropy measured by the Hahn-echo decay was numerically simulated taking into account the statistics and orientational distribution of the end-to-end vectors and their dependence on the extension ratio. As an example for a macroscopic distribution of local segmental anisotropy ^{1}H Hahn-echo decays was measured by the NMR-MOUSE® sensor in a stretched cross-linked natural rubber plate with circular cut in the middle.

The results were published in Solid State Nuclear Magnetic Resonance [5].

2.4. The possibility to measure an integrated dispersion of the longitudinal magnetization relaxation in the rotating frame in the presence of strongly inhomogeneous magnetic fields of the NMR-MOUSE® sensor was investigated by numerical simulations and experiments. It was shown that the method could be used for nondestructive measurements of heterogeneities of the large scale elastomers important for industrial applications.

A manuscript is in preparation related to this topic [18].

3. *Characterization of polymer networks by self-diffusion of penetrant molecules*

In many systems investigations of self-diffusion are an important source of information on molecular organization and interactions with the environment.

3.1. The local deformation of elastomer networks under the action of external forces can be investigated by measuring the self-diffusion tensor of small molecules incorporated into the network by swelling. The existence of the anisotropy in the diffusion coefficients of toluene was detected under compression for a series of network elastomers. The NMR parameters of ^{129}Xe diffusion in stretched cross-linked natural rubber were also investigated.

These results will allow us to characterize the inter-chain interactions and local segmental orientations and a paper on these topics is in preparations [19].

3.2. A new method to measure diffusion coefficients, D, using mobile NMR sensors was developed. At the core of this technique a sophisticated C++ program was written that allow the interpretation of the experimental data. The method was shown to be particularly useful for measuring the diffusion coefficient for solvent molecules in elastomers without the need for deuteration or measurements of the transverse relaxation rates. The self-diffusion coefficient of toluene in a cross-linked natural rubber samples was measured and correlated with the cross-link density. Finally, the method was applied to measure the diffusion anisotropy of free water in Achilles bovine tendon using a new mobile NMR-MOUSE® sensor with improved performances.

A paper describing these results was submitted to the Journal of Magnetic Resonance [10].

4. *Orientation of collagen fibrils and new magnetic resonance imaging contrast filters of ordered tissues*

4.1. The ^{1}H DQ filtered NMR signals of bound water were used to quantitatively determine the anisotropy of the residual dipolar couplings in tendon. The values of the residual dipolar couplings were obtained from the DQ build-up curves as well as the DQ-filtered spectra measured in the initial regime of the excitation/reconversion periods. At the magic angle the value of the residual dipolar coupling is different from zero that is a manifestation of a distribution of the collagen fibril directors around the macroscopic symmetry axis of the tendon. In the first approximation this distribution can be described by a Gaussian angular distribution function with a center of the distribution slightly shifted from the tendon axis. Moreover, for the first time, the distribution function based on a Legendre

polynomial expansion used for characterization of oriented polymer films and a fiber was shown to be suitable to obtain information about orientation of sheep tendon.

The method based on the DQ build-up curves described in this work can be used for a quantitative investigation of the anisotropy in different ordered tissues and to establish a correlation between the degree of orientation of the collagen fibrils and the biological functionality. Moreover, degeneration processes and injuries can be characterized by changes in the angular distribution of the fibrils. This method can be combined with magnetic resonance imaging procedures to measure the heterogeneities of the degree of orientation of various ordered tissues *in vivo*.

Parts of these results are in press in the Journal of Magnetic Resonance [8] and further results will be submitted to Physical Review Letters [12].

4.2. New dipolar filters for enhancing the contrast of magnetic resonance imaging of ordered tissues have been implemented. These filters use dipolar encoded longitudinal magnetization and double-quantum decay curves. The signal-to-noise ration and hence the resolution of the images are improved compared to the classical methods based on double-quantum build-up curves. The efficiency of the procedures has been demonstrated on sheep tendons.

A manuscript related to these results is in preparation [14].

5. Design of improved NMR sensor for oil exploration

The development of mobile NMR sensor with improved performances for well-logging it is an important topic for NMR applications. Moreover, development of new methods for characterization of oil and rocks are of extreme importance for well-logging. For both objectives the evaluation of the response of the NMR sensor is crucial. This response has to be simulated by a complex numerical procedure that takes into account the space distribution of static and radio-frequency fields and heterogeneity of the sample. Such software package suitable for many different situations was developed in C++ and its performance were tested solving various problems related to the optimization of the NMR sensor and to the implementation of new methods.

We estimate that there is the possibility to have one or more patents based on this general tool.

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