Conclusions

Multiple quantum (MQ) NMR spectroscopy has been used to investigate the dipole-dipole couplings in amorphous polymers. Various high resolution MQ and double quantum (DQ) NMR techniques under fast *magic angle spinning* (MAS) and low resolution static MQ techniques were compared with respect to application to polymers.

The theory for exciting MQ coherences under fast MAS and under static conditions has been unified for multiple-pulse sequences which are characterized by DQ Hamiltonian. It is shown that intensity of DQ coherence, which is used for estimating dipolar couplings, has the same form for MAS as well as for static experiments in the limit of two spin approximation. Initial part of the DQ build-up curve was used to evaluate dipolar couplings. In addition numerical simulations of intensities of DQ build-up curves confirm the theoretical predictions that POST C7 and C7 r.f. pulse sequences are more efficient than DRAMA and BABA r.f. pulse sequences.

The theoretical calculations show that the influence of finite switching times between r.f. pulses to the zero-order average Hamiltonian for BABA r.f. pulse sequence is small if the delays between these pulses are smaller than 0.5 μs, which is nowadays in commercial spectrometers good fulfilled. Care has to be taken for proper design of the multiple-pulse sequences especially under fast MAS. The timing of the pulses has to be symmetric with respect to the rotor period.

Proton experimental results on elastomers confirm the theoretical predictions that POST C7 as well as C7 r.f. pulse sequences are more efficient in comparison to BABA r.f. pulse sequence. DRAMA r.f. pulse sequence was not applicable on elastomers. It does not remove resonance offsets and chemical shift anisotropies (CSA) during excitation/reconversion period, which has dramatic influence to the DQ zero-order average Hamiltonian produced by this pulse sequence. It was also shown that ^{1}H DQ spectroscopy permits site-selective measurements of residual dipolar couplings between protons belonging to the same or to the different functional groups even for more complicated samples like natural rubber.

Measurements of the residual dipolar couplings in polybutadiene melt (PBM) under fast MAS conditions and without sample spinning show in the frame of experimental error the same results. In PBM the effect of rotation to the residual coupling is expected to be small because of no crosslinks present. It has to be noted that with such a comparison one has to be very careful especially for samples with higher crosslinking density. High spinning frequencies induce high centrifugal forces, which press the sample to the wall inside of the rotor. Due to this high pressure sample can be deformed and mobility of the crosslinks can be influenced. Hence, residual dipolar couplings for different functional groups can be different when comparing fast MAS and static experiment.

It is shown that high resolution MAS MQ experiment can be used for determining growing of the spin clusters. Number of correlated spins is increased with increasing excitation time. It was experimentally confirmed that also POST C7 can measure sizes of the spin clusters in Adamantane. Results are in the good agreements with the literature ([Gra97a, Gee99]) where C7 was used.

A thirty-two r.f. pulse sequence successfully excite up to the 6-th order of coherences in high crosslinked polybutadiene rubber (PBR) under static conditions. Gaussian distribution ([Bau85]) was not appropriate to measure sizes of the dipolar spin clusters in PBR. Its use is limited for large clusters bigger than: 6. Our attempt to fit higher order coherences using Gaussian distribution model shows the size of the clusters: 4, hence this is the confirmation that Gaussian model can not be used for PBR. Nevertheless, this experiment showed that both groups CH and CH_2 exhibit the same amount of correlated spins.

Problems of TPPI and 'hypercomplex' Fourier transformation are discussed in connection to DQ spectroscopy for various multiple-pulse sequences. It is shown that 'hypercomplex' acquisition may be preferred for C7 based r.f. pulse sequences but on the other hand for BABA and DRAMA r.f. pulse sequences TPPI acquisition is preferred.

Proton DQ NMR spectroscopy permits site-selective measurements of residual dipolar couplings belonging to the same or to the different functional groups. Another possibility to measure directly such couplings has been recently reported by Malveau et al. ([Mal97]). It exploits the indirect observation of protons through ^{13}C resonances in two-dimensional (2D) WISE experiment ([SR94, Eul00]). The advantage of site-selective DQ experiment with comparison to this conceptually relatively simple technique is that the acquisition of the signal from low abundant nuclei is avoided. Dipolar connectivities between different functional groups can be investigated also by 2D magnetization exchange spectroscopy in the short mixing-time regime ([Gas99]). However, for evaluating the data, a model of the spin topology is required. In comparison to DQ spectroscopy this is a disadvantage. DQ high resolution MAS as well as static DQ spectroscopy allows a model-free access to the ratio of the site-selective couplings when a spin-$^1\!/_2$ pair approximation is valid.

MQ as well as DQ spectroscopy are well established in modern NMR. They are not restricted to use only for ^{1}H systems. They can be extended also to other spin-$^1\!/_2$ nuclei. Recently published experiment based on C7 r.f. pulse sequence shows that modified C7 ([Hon99]) can be used to achieve even higher selectivity in INADEQUATE ([Ern87]) experiment. This with the connection to DQ techniques presented in this work might be used to measure connectivities between functional groups, which can not be distinguished with classical DQ spectroscopy.