

Advanced NMR Analysis of Polymers and Biomolecules

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Introduction

Nuclear magnetic resonance (NMR) is one of the most powerful tools in biology, chemistry, physics and medicine for the investigation of structure, morphology and dynamics of various classes of compounds. Few analytical techniques in science match, in either breadth or depth, the impact achieved by nuclear magnetic resonance [Gra1]. “Originated as an unexpected by-product of the quantum mechanics revolution [Rab1], NMR remained mostly a curiosity of the molecular beam community until Bloch, Purcell and their coworkers demonstrated the possibility of observing its manifestation in bulk [Rig1]. This in turn triggered the use of nuclear spins as tiny *spies* capable of characterizing the structure of organic molecules [Blo1], a feature that transformed NMR into one of the cornerstones of modern chemical and pharmaceutical research” [Fry1]. Over the years NMR undertook many other unforeseen applications: it became a common research tool in solid state chemistry and condensed matter physics; it afforded one of the few methods available for determining the structures of proteins and nucleic acids in their native solution state; and it expanded into medicine, both as an imaging, as well as a spectroscopy tool to study metabolism, diagnose malignancy, angiograph non-invasively, and reveal brain function [Gra1, Coh1, Cal1, Sch1, Cav1, Bux1]. A feature that distinguishes modern NMR from the few other techniques that might claim comparably wide impact areas of applicability is the fact that, broadly speaking, one common protocol underlies most of its very different applications. This protocol is multidimensional Fourier transform NMR, n D FT NMR, initially carried out along two axes [Jee1, Aue1] but eventually extended to the correlation of multiple spectral – and in the case of imaging, to the correlation of multiple spatial [Bux1, Man1] – domains. n D NMR seeks to measure, spread and correlate NMR evolution frequencies. This is not generally carried out by exciting spectral lines, but rather by manipulations in their Fourier conjugate space, i.e. in the time-domain.

The importance of one of the matter-investigation methods can be also quantified by considering the number of Nobel awards given to a specific domain in science. Nuclear magnetic resonance has thirteen Nobel awards, the last three ones being given in the last twenty years. Professor Richard Ernst got the Nobel Prize in 1991 mainly for introducing multidimensional NMR spectroscopy for the elucidation of complex molecular structures and the investigation of molecular dynamics, in unprecedented details. Later on, in 2002 Prof. Kurt Wüthrich received the Nobel Prize for applying the method developed in the laboratory

of Prof. Ernst to determine the 3D structure of proteins in solution. In 2003 Prof. Paul Lauterbur and Sir Peter Mansfield were awarded the Nobel Prize for the discovery of NMR tomography. It is evident now that NMR is one of the most versatile, non-invasive methods for investigating various states of matter.

The present work reports the results obtained by NMR spectroscopy and relaxometry on advanced polymers like ultra-high molecular weight polyethylene (UHMWPE), diblock copolymers, isotactic polypropylene / silica nanocomposite, porous polypropylene, and elastomers. Also the dynamic behaviour of lecithin in bulk and in geometrically confined states, and the morphological and molecular dynamics changes induced by hydration of hard α -keratin were investigated. Several new NMR methods were developed and applied to investigate advanced materials. For instance, multidimensional ultrafast spectroscopy was developed for the first time for solids under magic angle sample spinning (MAS) conditions. The *rotor synchronized stimulated echo* method is introduced as a new tool for the characterization of polymer chain dynamics. A modern procedure for interpreting proton spin-diffusion experiments for different polymer morphologies is also discussed.

The thesis is structured in seven chapters. The first one discusses the chemical site-specific dynamics of lecithin using ^{13}C spectroscopy, ^1H - ^{13}C wideline separation (WISE), ^1H - ^{13}C rotational echo double resonance (REDOR), spin-lattice relaxation in the rotating frame, ^{31}P wideline spectroscopy, and thermally polarized ^{129}Xe . Such a study using a combination of different advanced NMR methods was never reported before. A coherent picture that correlates the chemical sites and molecular dynamics resulted from this investigation.

The second chapter presents the correlation between the structure and the chain dynamics of polymethylmethacrylate-co-polystyrene (PMMA-co-PS) diblock copolymer. The domain sizes of each block were measured by ^1H spin-diffusion. The chain dynamics was investigated by ^{13}C spin-lattice relaxation time in the rotating frame. For the first time the correlation between quantitative morphology and chain dynamics was established based on these measurements.

The possibility to use a spectroscopic NMR method in combination with relaxometry is discussed in Chapter 3. The time evolution of the ^1H spectra edited by the stimulated echo for a rotor synchronized pulse sequence was used for measuring site-selective residual dipolar couplings in cross-linked natural rubber. A theoretical description of this method based on the evolution of the density operator was developed for an arbitrary value of the pulse flip angle. The method allows fast NMR experiments, using the Ernst-angle approach. This is of great

importance for the investigation of large series of elastomers samples, differing in cross-link density and filler content.

The Chapter 4 is related to the investigation of phase composition, chain dynamics and domain sizes for isotactic polypropylene (iPP) with silicon oxide nanoparticles. NMR spectroscopy of ^1H and ^{29}Si was used to study the SiO_2 network obtained by *in situ* conversion of polyethoxysiloxanes (PEOS) under various experimental conditions. The iPP/ SiO_2 nanocomposites, obtained by blending iPP with PEOS in different weight percentages, was characterized by ^1H wideline spectroscopy and ^1H spin-diffusion. The structural information was corroborated with mechanical and thermal properties. Moreover, these data are in agreement with SAXS and WAXS results reported by Prof. D.A. Ivanov at *Institut de Chimie des Surfaces et Interfaces*, Mulhouse (France).

In Chapter 5, the structure – property relationship was investigated for a series of experimental UHMWPE Dyneema[®] fibers with different tensile strengths. Proton wideline spectra under static and fast MAS (10 kHz), ^1H spin-diffusion, ^{13}C spectroscopy, ^{13}C - ^1H WISE, and T_1 edited ^{13}C spectra were used to characterize the changes in morphology and chain dynamics with the fibers drawing. Such a detailed investigation was performed for the first time on these materials. Moreover, the existence of an intermediate fraction was detected and its properties investigated. The voids induced in the process of fibers drawing were characterized with spectra of the thermal polarized ^{129}Xe .

The new method of ultrafast multidimensional NMR spectroscopy proposed by Prof. Frydman was extended to the field of solids under MAS in Chapter 6. It is expected for this new tool to find new applications especially for the study of dynamic processes. The possibility to apply exchange spectroscopy under ultrafast 2D conditions was explored for LASER-hyperpolarized ^{129}Xe in porous polymer membranes.

In Chapter 7, the morphological and molecular dynamics changes induced by hydration of hard α -keratin are evaluated. The fraction composition and side-chain dynamics were measured on Caucasian hair at different levels of hydration by ^1H wide-line spectra. The rigid and mobile domain sizes were determined by ^1H spin-diffusion using the initial-rate approximation in combination with the quasi-equilibrium ratio of the NMR signals.

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1 Characterization of local dynamics of lecithin by multi-nuclear NMR

1.1 Introduction

Molecular films of self-assembled single bilayer lipid membranes on solid planar supports [Cre1, Gro1, Nau1, Tam1] have attracted considerable attention due to their potential applications in biosensing and bioseparation as well as due to their interesting physical properties [Cor1, Goo1, Wan1, Sac1]. The function of these biocompatible molecular layers on solid substrates is associated with their structure, packing, and dynamics. A recent ^2H NMR study by Zalar *et al.* [Zal1, Zal2] on liquid crystal films in porous hosts has suggested that upon reducing the effective layer thickness to an order of one molecular length or even less, a deviation from the order and dynamics of three-dimensional (3D) bulk phase to 2D-liquid or 2D-gas behavior occurs. In the light of these investigations and also due to some similarities that liquid crystals have with lipid molecules [Xue1] it is interesting to study ultrathin films of phospholipids. Furthermore, knowledge of the role that the solid substrate plays with regard to the lipid molecular ordering and dynamics may serve as important information in the manufacture of biosensors. Hence, the study of the dynamics of lipid molecules at various surface coverage, ranging from bulk-like thick films to submonolayer effective thickness, is essential for understanding the properties of lipid films at a molecular level, and our work is aimed in this direction. Recently, there were reported ^1H NMR studies of lipid films with monolayer to a submonolayer effective thickness absorbed on hydrophilic porous substrates (Anopore membranes), with varying size of confinement [Jag1]. The experimental techniques involved excitation of multipolar spin states such as by double-quantum (DQ) and triple-quantum (TQ) coherences and measuring the splitting of DQ edited spectra. The slopes of the DQ, and TQ buildup curves, and the splitting $\Delta\nu_{\text{DQ}}$ of the DQ edited spectra are related to the average values of the residual dipolar couplings and are remarkably lower for the films compared to those in the bulk, indicating faster dynamics in the films. The existence of dynamic heterogeneities along the backbones of the grafted molecules is put into evidence only indirectly in these experiments as opposed, for instance, to those performed on poly(dimethylsiloxane) layers chemically attached to the surface of hydrophilic silica [Wan2].

The molecular dynamic heterogeneity of monolayer to submonolayer thin lecithin films confined to submicron cylindrical pores was investigated by ^1H magnetization exchange nuclear magnetic resonance [Bud1]. In this experiment a z -magnetization gradient was generated by a double-quantum dipolar filter. The magnetization-exchange decay and buildup curves were interpreted with the help of a theoretical model based on the approximation of a one-dimensional spin-diffusion process in a three-domain morphology. The dynamic heterogeneity of the fatty acid chains and the effects of the surface area per molecule, diameter of the pores and temperature were characterized with the help of local spin-diffusion coefficients. The effect of various parameters on the molecular dynamics of the mobile region of the fatty acid chains was quantified by introducing an *ad hoc* Gaussian distribution function of the ^1H residual dipolar couplings. For the lipid films investigated in this study, the surface induced order and the geometrical confinement affect the chain dynamics of the entire molecule. Therefore, each part of the chain independently reflects the effect of surface coverage, pore size, and temperature.

In this chapter we discuss original results related to the characterization of the local dynamics in bulk lecithin. They provide us a much deeper understanding of the changes induced by geometrical confinement in the local dynamics of lipid films, so a better understanding of the behaviour of artificial and biological membranes is gained. NMR experiments based on ^{31}P spectroscopy, ^{13}C high-resolution spectroscopy under magic angle spinning (MAS), $^{13}\text{C} - ^1\text{H}$ wideline separation (WISE) and rotational echo double resonance (REDOR) experiments are presented. Moreover, the results obtained from preliminary experiments with thermally and hyperpolarized ^{129}Xe are described.

1.2 Experimental

Samples. The lipid used in the present study is a 99.0 % purity egg yolk lyophilized powder, also known as 1,2-diacyl-*sn*-glycero-3-phosphocholine, purchased from Sigma-Aldrich Chemie GmbH, Germany. The chemical structure of this egg yolk lecithin along with the labeling of different ^{13}C sites present in the molecule are shown in Fig. 1.1a. The molecule consist of a rather polar “head group” and comparably apolar residues (Fig. 1.1b). In the solid state, the molecule tends to orientate in a distinct way, i.e., lipophilic tails and hydrophilic head group take a separate, packed arrangement. The presence of the carbon-carbon double-bonds in one of the hydrocarbon chains leads to a kink in the chain.

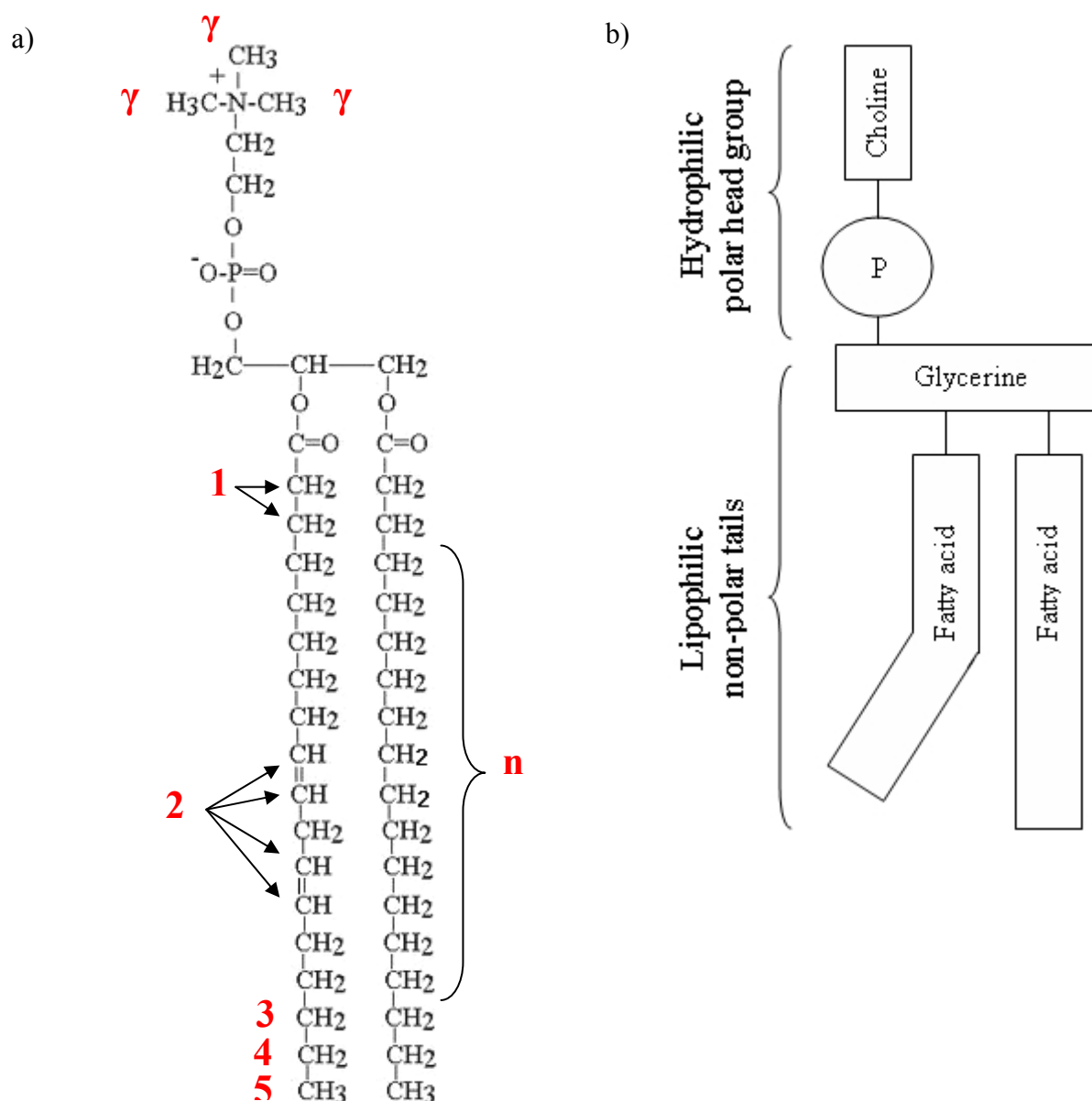


Fig. 1.1 a) Chemical structure of the egg yolk lecithin $\geq 99\%$ purity (1,2-diacyl-*sn*-glycero-3-phosphocholine). The positions of ^{13}C along the molecule are labeled by 1, 2, 3, ..., n for the acyl chains and by γ for the methyl groups in the hydrophilic head. b) The hydrophobic and hydrophilic parts of the lecithin molecule.

^{13}C NMR spectroscopy by ^1H - ^{13}C cross-polarization under MAS. The ^{13}C solid-state NMR experiments were conducted using a Bruker DSX 500 spectrometer ($B_0 = 11.75$ T) at a ^{13}C resonance frequency of 125.84 MHz and a ^1H resonance frequency of 500.44 MHz. Measurements were made at ambient temperature ($T = 295$ K) under fast magic angle sample spinning (MAS) of 10 kHz. For all experiments, a double-resonance Bruker MAS NMR probehead and 4 mm diameter zirconia rotors were used to hold the samples. The rotor inside the MAS NMR probehead makes an angle $\theta = 54.7^\circ$ (the so called *magic angle*) with respect to the $\mathbf{B}_0$ magnetic field.

The standard cross-polarization (CP) measurements under MAS [Pin1, Dem1, Har1], whose pulse sequence is described in Fig. 1.2, utilizes a ^1H 90° pulse length of $7\ \mu\text{s}$ at 7 dB attenuation, and a contact time of 3 ms on both ^1H and ^{13}C channels, with a power attenuation of 7 dB and 8.5 dB respectively, allowing the heteronuclear cross-polarization transfer. The time dependent signal of ^{13}C is recorded under high power decoupling using the broadband pulse sequence TPPM20 (two-pulse phase modulation), consisting of a train of 180° pulses on the ^1H channel, with a phase difference of 20° between the subsequent pulses [Tha1]. The power attenuation used for the 180° decoupling pulses is 4 dB and the length of the pulses is $10\ \mu\text{s}$. The dead time of the spectrometer was on the order of $5.5\ \mu\text{s}$.

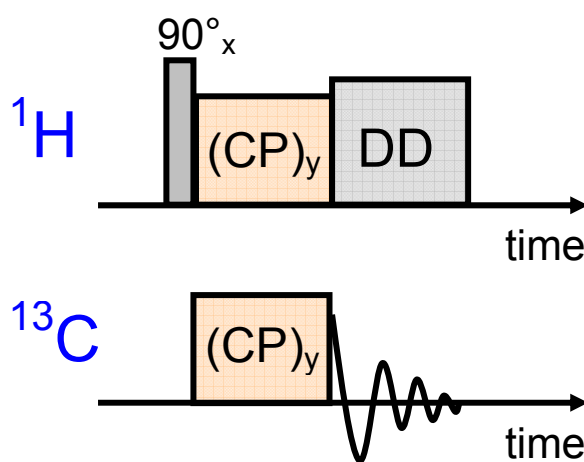


Fig. 1.2 Standard heteronuclear cross-polarization pulse sequence. After a 90° pulse on the ^1H channel, the polarization transfer from the ^1H nuclei to the ^{13}C nuclei takes place and the ^{13}C signal is recorded in the presence of a ^1H - ^{13}C heteronuclear dipolar decoupling.

$^{13}\text{C} - ^1\text{H}$ WISE. The pulse sequence used for the two-dimensional wide-line separation (WISE) NMR experiments is displayed in Fig. 1.3. It starts with a 90° radio-frequency pulse of $7\ \mu\text{s}$ length at 13 dB power attenuation on the ^{13}C channel followed, after a short delay of $30\ \mu\text{s}$, by a 90° pulse of $8.4\ \mu\text{s}$ at 7dB power attenuation on the proton channel. Coming next is an incremented proton evolution period (t_1) which starts with the initial value of $1\ \mu\text{s}$ and is increased in 128 steps, always by the same value of $1\ \mu\text{s}$. By means of Hartmann-Hahn cross polarization from protons to carbons, the proton magnetization at the end of the evolution period is transformed into amplitude modulation of the ^{13}C signal, which is probed in the t_2 domain of the experiment, in the presence of a ^1H - ^{13}C heteronuclear dipolar decoupling. The contact pulse (CP) has a length of 3 ms on both ^1H and ^{13}C channels, using a power attenuation of 7 dB and 13 dB respectively. The ^{13}C free induction decay (FID) is detected under high power decoupling using the TPPM20 pulse sequence.

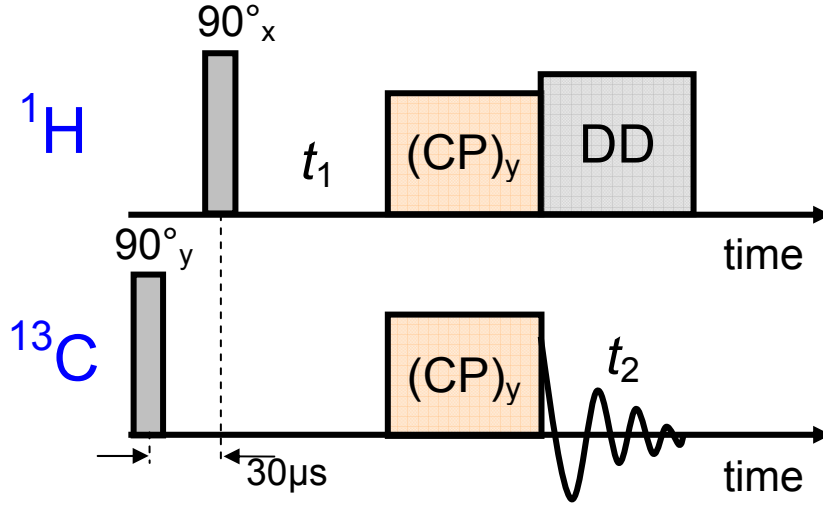


Fig. 1.3 Two-dimensional ^{13}C - ^1H WISE pulse scheme.

$^{13}\text{C} - ^1\text{H}$ REDOR. The rotational echo double resonance (REDOR) technique was introduced by Schaefer and coworkers [Gul1], and relies on the fact that the effect of the dipolar interaction between two spins on the rotational echo can be manipulated by π -pulses. The dephasing of magnetization of one spin involved in dipolar coupling to another heteronucleus in the presence and absence of these π -pulses, and subsequent refocusing as a function of the magic angle spinning frequency, leads to a variation of resonance intensities. This intensity variation is related to the dipolar coupling constant.

The REDOR experiments were carried out with a Bruker DSX 500 spectrometer, under 10 kHz magic angle sample spinning condition, using the pulse scheme presented in Fig. 1.4. A first spectrum is obtained using a standard cross polarization pulse sequence with just a single π -pulse on the observed nucleus (*e.g.* ^{13}C) in the middle of the evolution period. During this period, the observable magnetization evolves under the influence of the chemical shifts and the heteronuclear dipolar interaction. The π -pulse refocus both interactions, leading to a signal S_0 during the acquisition period. A second spectrum is obtained with an additional train of π -pulses on the dipolar-coupled spin (*e.g.* ^1H). Using a 4 dB power attenuation, selective 180° pulses are applied to ^1H spins at one-half and full rotor periods after the initial $^1\text{H} - ^{13}\text{C}$ cross-polarization. These pulses affect the observed signal by preventing rotational refocusing of the dipolar interaction. The magnetization is therefore not completely refocused, and the signal intensity drops by an amount ΔS . For weak dipolar coupling, the change in signal intensity is related to the distance between the coupled spins by equation:

$$\frac{\Delta S}{S_0} = A \cdot (N\tau_r)^2 D^2 \quad (1.1)$$

where N is the number of rotor cycles during the evolution period, τ_r is the rotor period (the inverse of spinning speed), D is the dipolar coupling (in Hz), and A is a dimensionless constant (taking different values for different functional groups CH, CH₂ and CH₃). Measurement of D can be used to calculate internuclear distance (r) according to Eq. 1.2:

$$D = \left(\frac{\mu_0}{4\pi} \right) \frac{\gamma_I \gamma_S \hbar}{2\pi r^3} \quad (1.2)$$

where γ_I and γ_S are the gyromagnetic ratios for the two heteronuclear spins involved, and $\hbar$ is Planck's constant divided by 2π . This experiment therefore yields the internuclear distance, which for an isolated spin pair can be determined to an accuracy of around ± 0.1 Å.

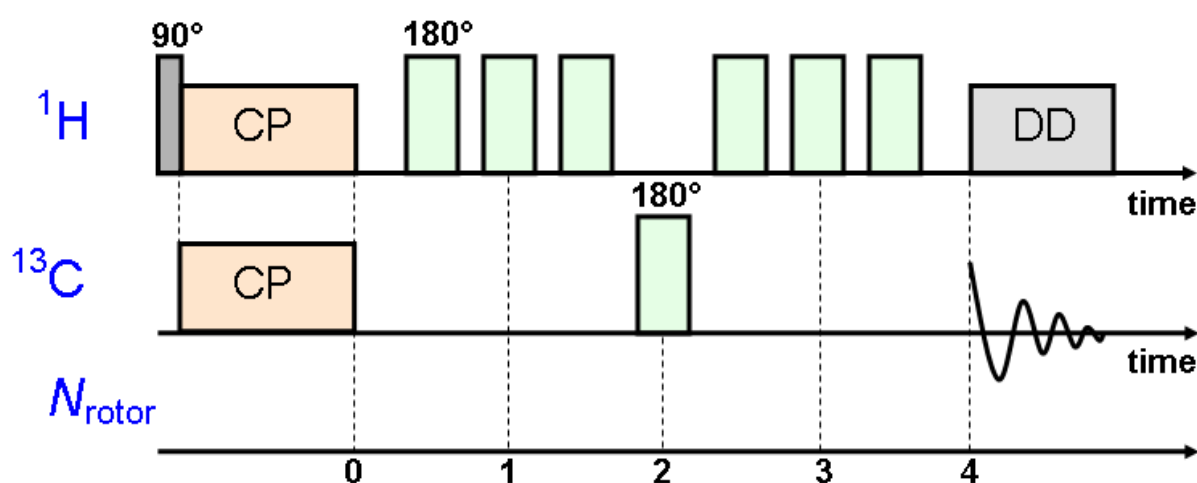


Fig. 1.4 REDOR pulse scheme used to measure the ¹³C-¹H residual dipolar couplings.

¹³C $T_{1\rho}$. Carbon-13 longitudinal magnetization relaxation in the rotating frame ($T_{1\rho}$) was measured with a Bruker DSX 500 spectrometer using a standard pulse scheme as described in Fig. 1.5. After the initial ¹H – ¹³C cross polarization, a spin-lock pulse is applied on the ¹³C

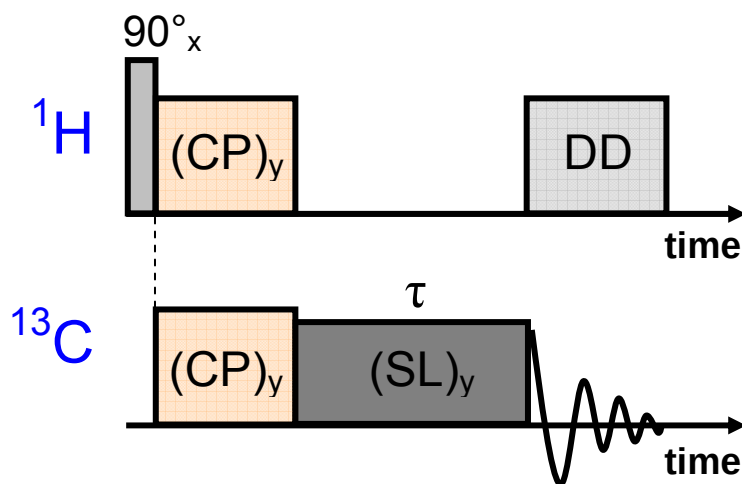


Fig. 1.5 The pulse scheme used to record the ¹³C longitudinal magnetization relaxation in the rotating frame.

channel, whose length τ is systematically increased. The shortest value of this spin-lock pulse was 10 μs and the highest one was 5 ms.

^{31}P MAS spectroscopy. The static ^{31}P NMR spectra of bulk lecithin were acquired with a Bruker DSX 500 spectrometer, operating at a ^{31}P resonance frequency of 202.58 MHz. A simple $\pi/2$ pulse excitation scheme was used, the length of the 90° pulse being 4 μs at a power attenuation of 6 dB. A 5 s recycle delay has been set, and the dead time of the spectrometer was in the 5.5 μs range.

Thermally polarized ^{129}Xe spectroscopy. Thermally polarized ^{129}Xe NMR spectrum was measured for bulk lecithin using a Bruker DSX 200 spectrometer at 55.33 MHz xenon resonance frequency. The measurement was done at room temperature in a home-made high-pressure sapphire tube, at a xenon gas pressure of 20 bar. In order to reduce the longitudinal relaxation rate of xenon gas, the tube was also loaded with O_2 at 5 bar. The recycle delay was reduced to the value of 10 s. The bulk lecithin was first introduced in a 5 mm diameter glass tube and then this tube has been inserted into the sapphire tube (Fig. 1.6), in order to avoid the contamination of the sapphire tube. A single 90° pulse excitation was used to record the xenon signal. The length of the 90° pulse was 70 μs at a power attenuation of 13 dB.

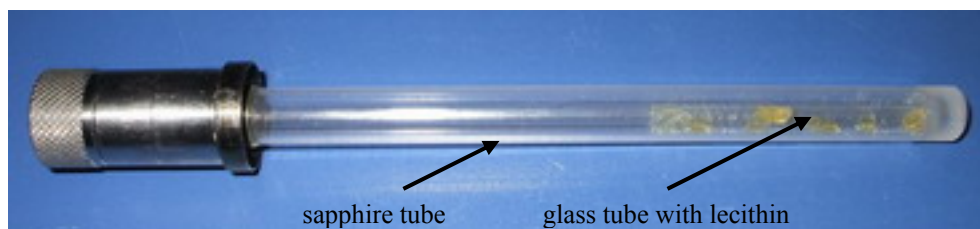


Fig. 1.6 The experimental setup for the measurement of the thermally polarized ^{129}Xe spectrum of bulk lecithin.

Hyperpolarized ^{129}Xe spectroscopy. The hyperpolarized ^{129}Xe NMR experiments were done using a hyperpolarizer instrument (built by Prof. Dr. Stephan Appelt at Forschungszentrum Jülich) connected to a Bruker DSX 200 spectrometer. (For a more detailed description of the hyperpolarizer instrument and its functionality, please see Chapter 6.) A simple $\pi/2$ pulse excitation scheme was used; the length of the pulse was 65 μs at a power attenuation of 13 dB. The spectrum was measured with 64 scans, in a total acquisition time of about 10 min. The pressure of the hyperpolarized xenon gas was 6 bar and the flow rate 300 cm^3/min .

1.3 Results and discussion

1.3.1 Carbon-13 CP-MAS spectrum of bulk lecithin

The cross polarization under magic angle spinning (CP-MAS) method was used to record ^{13}C high-resolution spectrum for bulk lecithin. This spectrum is shown in Fig. 1.7. From this spectrum it is evident that ^{13}C chemical shift is very sensitive to the location of methylene and methyl groups along the lecithin molecule.

The lowest chemical shielding interaction is detected for the CH_3 groups present at the end of the acyl chains (denoted $^{13}\text{C}_5$ in Fig. 1.1a), whereas the highest chemical shift corresponds to the methyl groups in the hydrophilic polar head of lecithin (denoted $^{13}\text{C}_\gamma$ in Fig. 1.1a). The peak corresponding to the $^{13}\text{C}_\gamma$ nuclei is broader than that one of $^{13}\text{C}_5$ nuclei, showing that the molecular motion is different for the CH_3 groups from the hydrophilic polar head and those from the lipophilic fatty acid chains.

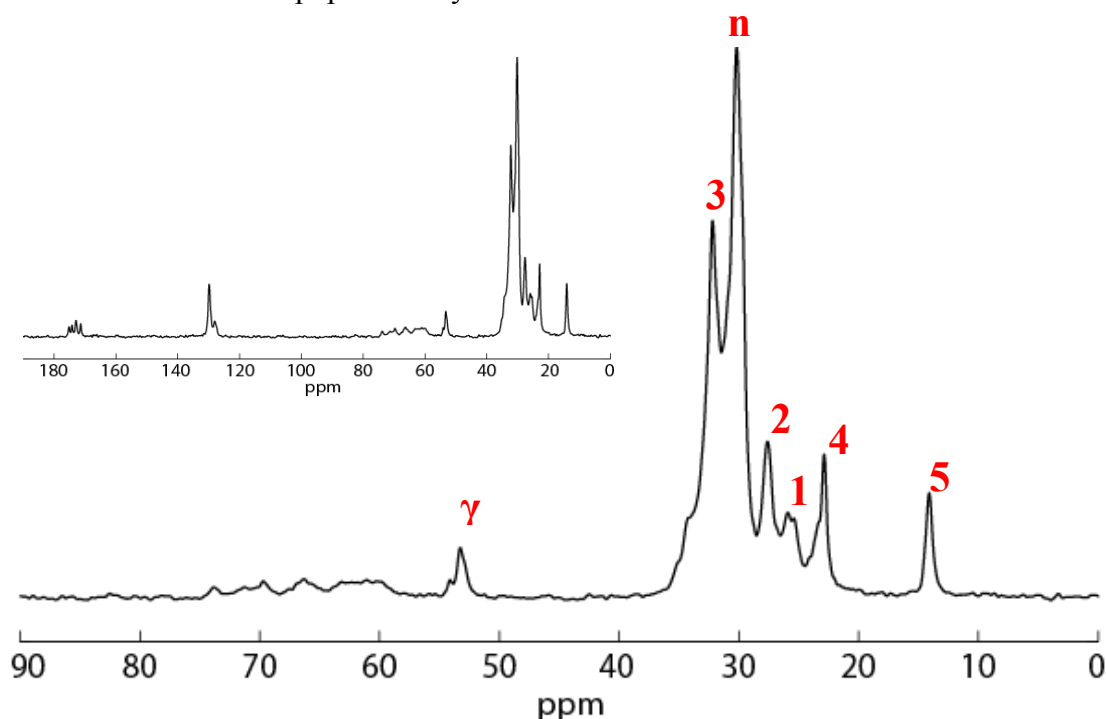


Fig. 1.7 Carbon-13 CP-MAS spectrum measured with a Bruker 500 DSX spectrometer, at 10 kHz sample spinning. The full spectrum is shown in the upper left-hand side, and the region of interest 0 - 90 ppm at the bottom. The resonance frequencies corresponding to different ^{13}C positions along the lecithin molecule (see Fig. 1.1a) are assigned.

The spectrum in Fig. 1.7 shows also that the ^{13}C chemical shift of the methylene groups in the acyl chains depends on the position along these mobile chains. The highest intensity in the spectrum is given by the twelve magnetically equivalent $^{13}\text{C}_n$ nuclei present along the straight lipophilic non-polar tail. All the peaks have a symmetric shape corresponding to an average ^{13}C chemical shift anisotropy (CSA) due to the local motions.

1.3.2 ^{13}C - ^1H WISE spectrum of bulk lecithin

A two dimensional wideline separation (WISE) spectrum is shown in Fig. 1.8. The linewidths of the different proton slices corresponding to different ^{13}C position along the lecithin molecule are different, suggesting that the molecular motions affect the local homonuclear dipolar interactions of protons. A short value of the contact pulse for the initial cross polarization transfer was used, a value that inhibits the spin-diffusion process and therefore, the slices carry local dynamics information.

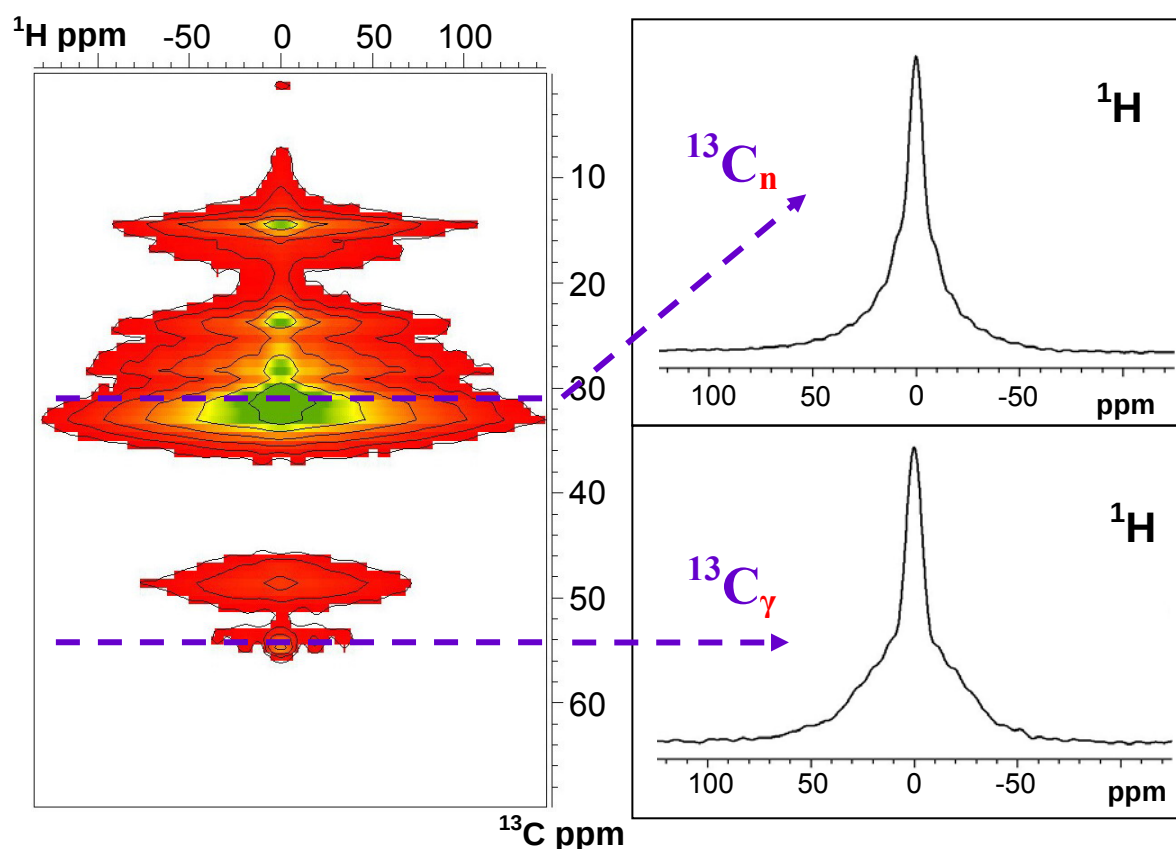


Fig. 1.8 The WISE spectrum for bulk lecithin measured at room temperature at 500 MHz proton frequency and 125.8 MHz ^{13}C frequency. On the right side, two proton slices from the WISE 2D spectrum are shown at the chemical shift positions of $^{13}\text{C}_n$ (from the methylene groups along the fatty acid chains) and of $^{13}\text{C}_\gamma$ (from the methyl groups in the choline head).

The linewidth of the ^{13}C slices from the WISE spectrum, related to the proton dynamics, are shown in Fig. 1.9 as a function of the position of the ^{13}C nuclei in the lecithin molecule. The fastest proton local dynamics is revealed by the C_nH_2 groups in the acyl chains. The more restricted dynamics is shown by the $\text{C}_\gamma\text{H}_3$ groups in the choline head. The dynamics of the protons for $\text{C}_{(5)}\text{H}_3$ is roughly the same as for $\text{C}_{(4)}\text{H}_2$, $\text{C}_{(3)}\text{H}_2$ and $\text{C}_{(1)}\text{H}_2$. The acyl chain with the double bond shows a hindered proton dynamics along the full chain with a relatively weak heterogeneity along the chain. This is obvious from Fig. 1.9, where the linewidth of the $\text{C}_{(1)}\text{H}_2$ is slightly larger than that of $\text{C}_{(5)}\text{H}_3$.

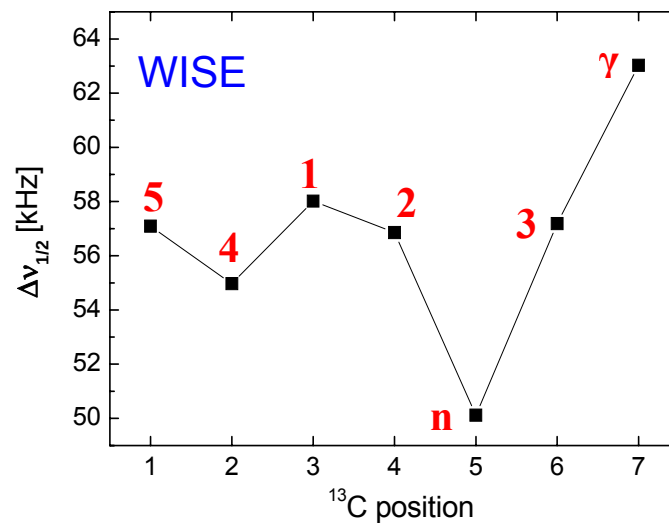


Fig. 1.9 Peak linewidth at half intensity for different slices from WISE 2D spectrum for different positions of ^{13}C in the bulk lecithin.

1.3.3 ^{13}C - ^1H REDOR of bulk lecithin

Residual heteronuclear dipolar couplings of ^{13}C spins coupled to protons were measured using the rotational echo double resonance (REDOR) method [Gul1]. The pulse sequence for these measurements is shown in Fig. 1.4. The lecithin sample was rotated by MAS at a rotor frequency of 10 kHz.

The buildup curves shown in Fig. 1.10 were measured for each non-equivalent position of ^{13}C nuclei along the lecithin molecule. ^{13}C - ^1H residual dipolar couplings are affected by the local molecular motions. The values of these couplings ($D_{^1\text{H}-^{13}\text{C}}$) along the lecithin molecule are derived from the fit of the initial part of REDOR buildup curves with a polynomial function in $N\tau_r$, i.e.,

$$\frac{\Delta S}{S_0} = A_1 \cdot (N\tau_r)^2 D_{^1\text{H}-^{13}\text{C}}^2 - A_2 \cdot (N\tau_r)^4 D_{^1\text{H}-^{13}\text{C}}^4 + \dots \quad (1.3)$$

The parameter A_1 in Eq.1.3 depends on the functional groups CH, CH₂ and CH₃. So in an approximation by considering only the first term in Eq. 1.3 for the fit of the experimental curves, we can write the following relationships according to the functional groups present in lecithin:

$$\frac{\Delta S}{S_0} = \frac{16}{15} \cdot (N\tau_r)^2 D_{^1H-^{13}C}^2, \text{ for CH groups} \quad (1.4a)$$

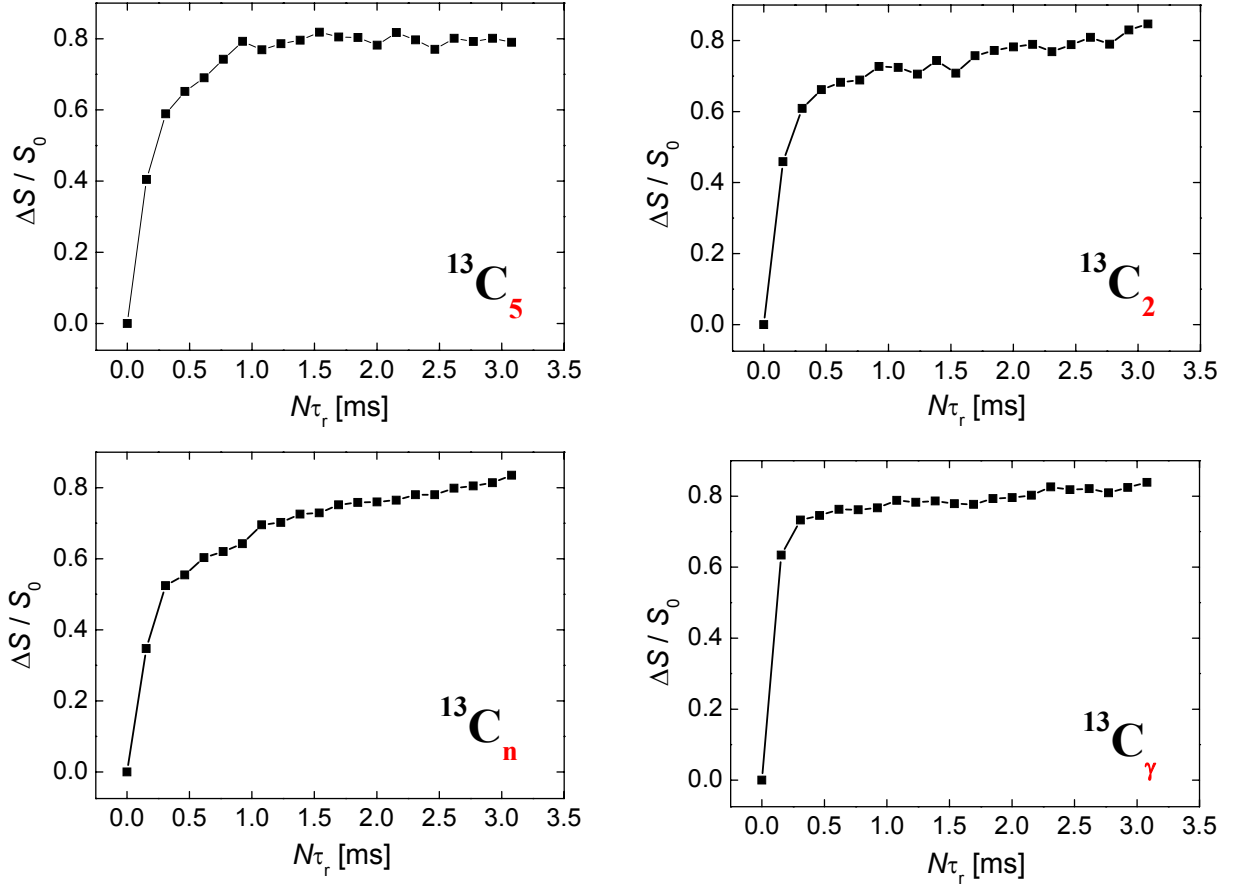


Fig. 1.10 $^{13}\text{C} - ^1\text{H}$ REDOR buildup curves for different ^{13}C positions in bulk lecithin are shown. The ^{13}C high-resolution signals $\Delta S/S_0$ are represented as a function of rotor period τ_r .

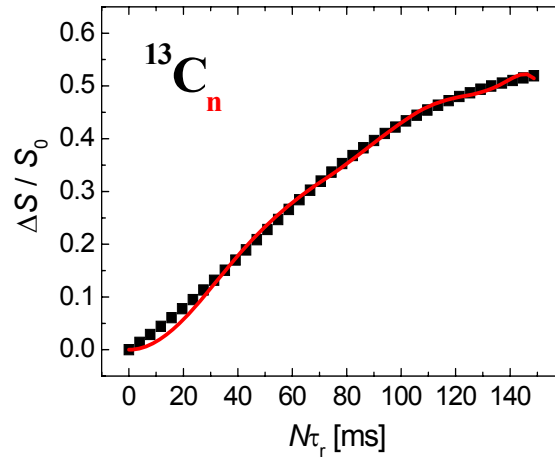


Fig. 1.11 Polynomial fit (red continuous line) of the experimental REDOR buildup curve (squares) corresponding to $^{13}\text{C}_n$ nuclei.

$$\frac{\Delta S}{S_0} = \frac{32}{15} \cdot (N\tau_r)^2 D_{1H-13C}^2, \text{ for CH}_2 \text{ groups} \quad (1.4b)$$

$$\frac{\Delta S}{S_0} = \frac{48}{15} \cdot (N\tau_r)^2 D_{1H-13C}^2, \text{ for CH}_3 \text{ groups} \quad (1.4c)$$

The quality of the fit with the above polynomial is shown in Fig. 1.11 for REDOR buildup curve of $^{13}\text{C}_n$. The values of residual heteronuclear dipolar couplings measured with the REDOR experiment as a function of ^{13}C sites in bulk lecithin are shown in Fig. 1.12. These results show a striking resemblance with those presented in Fig. 1.9. That shows that the local molecular motions that include local reorientation of CH_3 groups, the rotations and vibrations of CH_2 , and also backbone fluctuations affect in a similar manner the homonuclear proton dipolar couplings (WISE) and the heteronuclear $^{13}\text{C} - ^1\text{H}$ dipolar couplings (REDOR).

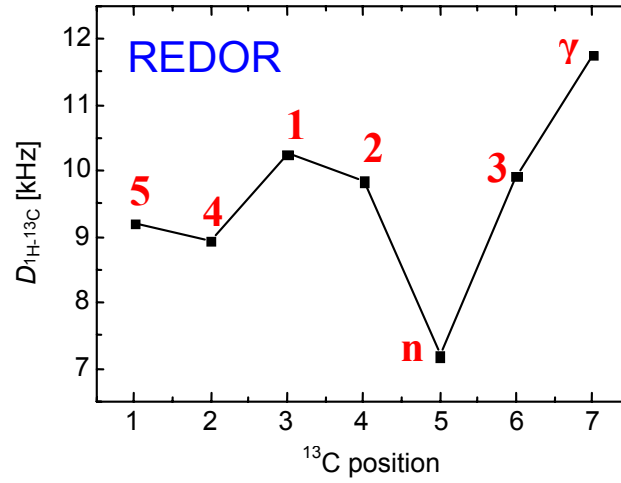


Fig. 1.12 Heteronuclear residual dipolar couplings D_{1H-13C} for different ^{13}C sites along the lecithin molecule.

1.3.4 Carbon-13 $T_{1\rho}$ in bulk lecithin

^{13}C longitudinal magnetization relaxation in the rotating frame ($T_{1\rho}$) was measured with a standard pulse sequence using a spin-lock pulse (see Fig. 1.5). The magnetization decay curves ($M(\tau)$) shown in Fig. 1.13 are all mono-exponential and therefore, could be fitted by the relationship:

$$M(\tau) = M(0) \cdot \exp(-\tau / T_{1\rho}) \quad (1.5)$$

The values of the ^{13}C longitudinal magnetization relaxation rate ($1/T_{1\rho}$) are shown in Fig. 1.14 for different positions of ^{13}C along the lecithin molecule. The mechanism of relaxation in the rotating frame could be related to the heteronuclear dipolar couplings $^{13}\text{C} - ^1\text{H}$ and the anisotropy of the chemical shift of ^{13}C .

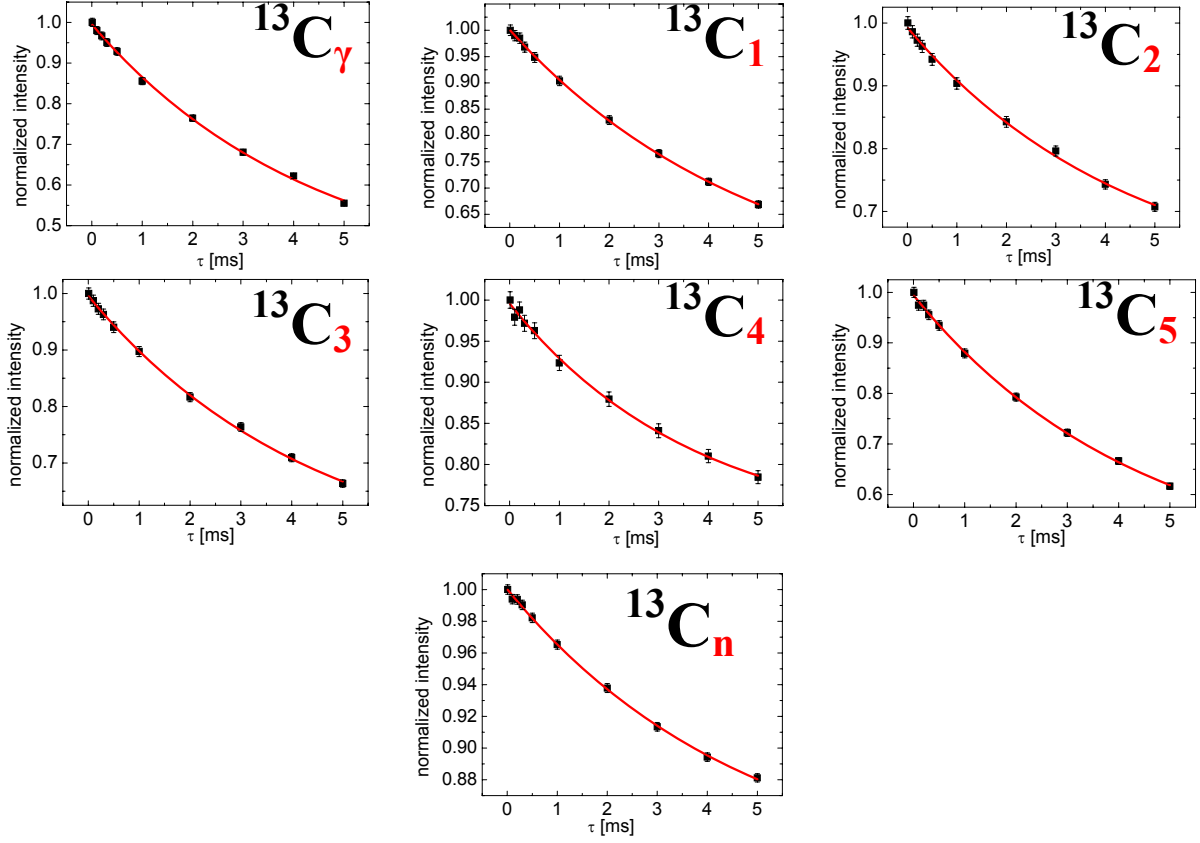


Fig. 1.13 ^{13}C longitudinal magnetization decay in the rotating frame measured in a high-resolution MAS experiment at 10 kHz for different sites of ^{13}C in bulk lecithin at room temperature.

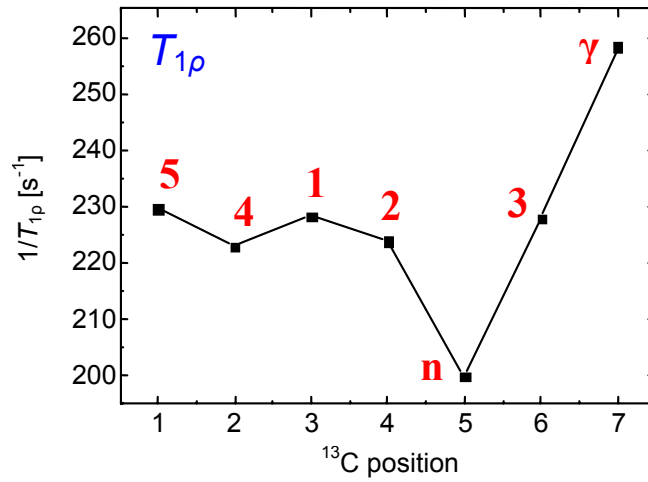


Fig. 1.14 Longitudinal magnetization relaxation rates $1/T_{1\rho}$ for bulk lecithin at different positions of ^{13}C .

It is evident that $1/T_{1\rho}$ changes with the position of ^{13}C in a manner similar to the heteronuclear residual dipolar couplings as measured by REDOR (see Fig. 1.12). This leads to the conclusion that $1/T_{1\rho}$ is related to the $^{13}\text{C} - ^1\text{H}$ heteronuclear dipolar couplings and therefore one can write:

$$\frac{1}{T_{1\rho}} \sim D_{^1\text{H}-^{13}\text{C}} \quad (1.6)$$

1.3.5 ^{31}P spectra in bulk lecithin

The local dynamics of the lecithin molecule can be investigated using the effect of rotations and vibrations on ^{31}P spectrum. In general, ^{31}P spectra are non-symmetric due to the presence of a strong chemical shift tensor. The NMR quantities that can be derived from the ^{31}P spectrum are the isotropic value (σ_i) of the chemical shift (CS), the anisotropy of CS, i.e., $\Delta\sigma = \sigma_{33} - \sigma_i$, and asymmetry $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \sigma_i)$. Local dynamics of the choline head of lecithin affects the shape of the ^{31}P spectrum.

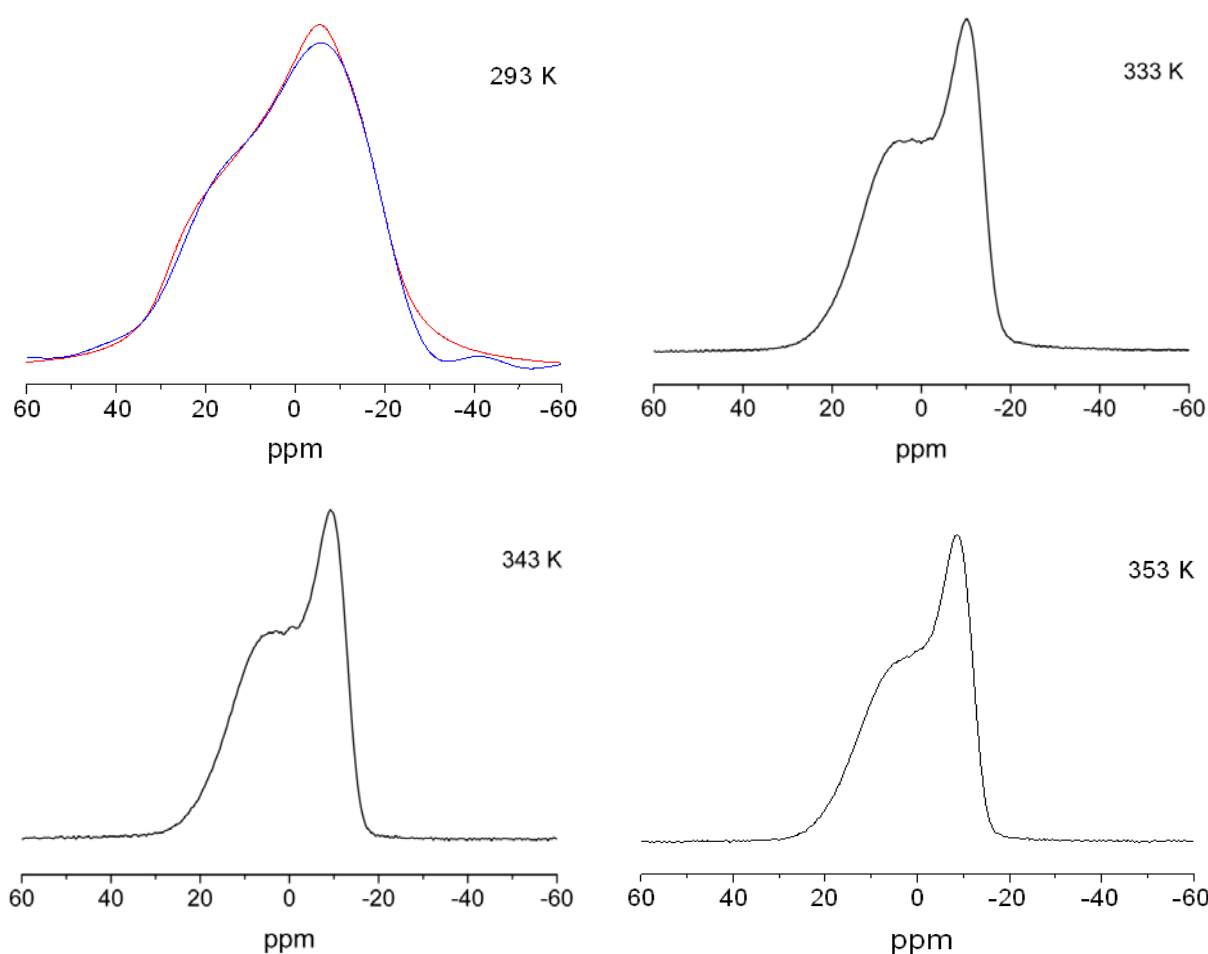


Fig. 1.15 ^{31}P NMR spectra of static bulk lecithin at different temperatures. The spectrum at $T = 293\text{ K}$ was fitted with “dmfit” program [Mas1], taking into account the anisotropy of the chemical shift and the asymmetry parameters.

The ^{31}P spectra for the bulk lecithin under static condition at different temperatures are shown in Fig. 1.15. It is evident that, as the temperature increases, the spectrum becomes narrower, but remains asymmetric. That proves that local dynamics of the functional groups surrounding ^{31}P is highly anisotropic. The parameters of the chemical shift tensor are obtained

from the fits of the experimental spectra using the “dmfit” program [Mas1]. An example of such fit is shown in Fig.1.15, for $T = 293$ K. The values of $\Delta\sigma$ and η as a function of temperature are shown in Table 1.1.

Tabel 1.1 The anisotropy and asymmetry parameters of ^{31}P chemical shift

T [K]	$\Delta\sigma$ [ppm]	η
293	27.59	0.52
333	20.03	0.14
343	19.25	0.19
353	18.09	0.19

The temperature dependence of $\Delta\sigma$ is shown in Fig. 1.16. A quasi-linear decrease in the anisotropy parameter is detected as a function of temperature. From the above results it is difficult to identify the specific local dynamics that lead to the narrowing of the spectra.

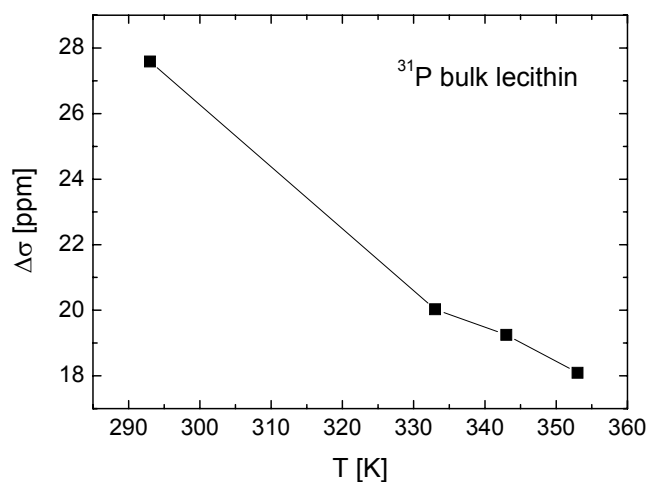


Fig. 1.16 The temperature dependence of the chemical shift anisotropy ($\Delta\sigma$) evaluated by fitting the ^{31}P spectra shown in Fig. 1.15.

1.3.6 Thermally polarized and hyperpolarized ^{129}Xe for investigation of bulk lecithin

The thermally polarized ^{129}Xe NMR spectrum of bulk lecithin is shown in Fig. 1.17. The peak corresponding to the free xenon gas and the peak of xenon absorbed in the lecithin show a fine structure. A possible interpretation is that this structure is due to the shift of the xenon resonance frequency caused by the magnetic susceptibility effect at the glass tube wall. From the ^{129}Xe spectrum it is evident that the signal of xenon absorbed in bulk lecithin is broadened compared to the signal of the free gas. This is due to the longer correlation time for the xenon-atom motions in bulk lecithin. If the xenon atoms are distributed along the fatty chains, the

atoms closer to the heavy hydrophilic part will lead to a broader xenon peak. The highly mobile part of the bulk lecithin represented by the acyl chains should lead to a narrow peak. Such structure of the spectrum is not clearly evident from Fig. 1.17 probably due to a continuous change in the xenon-atom mobility and possible fast exchange between different positions.

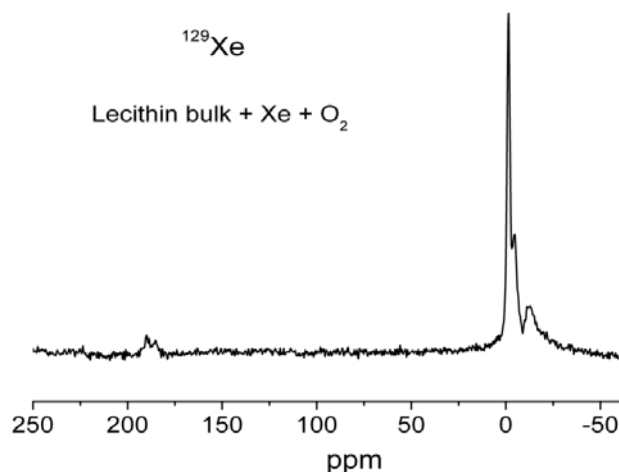


Fig. 1.17 Thermally polarized ^{129}Xe NMR spectrum of bulk lecithin. The position of the free gas was taken as reference (0 ppm) for the chemical shift scale. The signal of ^{129}Xe in bulk lecithin is shown at about 190 ppm.

The same experiment as above was made using LASER hyperpolarized ^{129}Xe gas. Now the bulk lecithin was introduced directly inside the sample holder and exposed to a continuous flow of hyperpolarized ^{129}Xe gas. The NMR spectrum is shown in Fig. 1.18. No structure of the free-Xe signal and the Xe gas absorbed in bulk lecithin is evident. Again, the xenon peak of absorbed gas does not show the presence of the broad and narrow signals, but has a super-Lorentzian shape. This can be explained again by the rapid exchange between different xenon atoms absorbed in lecithin, between less mobile and more mobile regions of acyl chains.

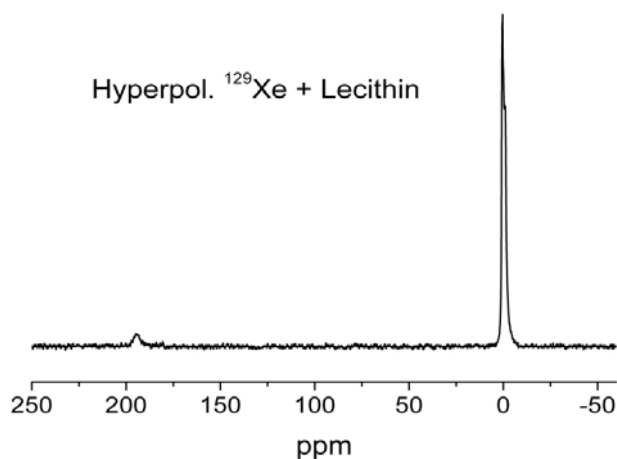


Fig. 1.13 Hyperpolarized ^{129}Xe NMR spectrum of bulk lecithin. The spectrum was measured with 64 scans in a total acquisition time of about 10 min. The pressure of the Xe gas was 6 bar, and the flow rate was $300\text{ cm}^3/\text{min}$.

1.4 Conclusions

Classical and advanced ^1H , ^{13}C , ^{31}P , ^{129}Xe NMR was used for characterization of bulk lecithin. The acquired information is of great importance for the forthcoming studies on the behavior of lecithin in a confined environment.

The heterogeneity of local motions of different functional groups along the bulk lecithin was measured by various NMR methods under static and magic angle spinning conditions. The residual homonuclear (^1H) and heteronuclear ($^{13}\text{C} - ^1\text{H}$) were measured using $^{13}\text{C} - ^1\text{H}$ WISE, $^{13}\text{C} - ^1\text{H}$ REDOR and ^{13}C $T_{1\rho}$ techniques. All these results correlate very well with each other. These three different methods yield quantitatively similar values of residual dipolar couplings along the lecithin molecule. As expected the fatty chains show the more intense molecular motion, whereas the hydrophilic polar head shows a more hindered local dynamics.

Spectra of ^{31}P reveal, as expected, a line shape strongly affected by the chemical shielding tensor. These results can open the possibility to investigate the effects of geometrical confinement for the lecithin.

For the first time thermally polarized and LASER hyperpolarized ^{129}Xe was used in an attempt to see the value of this method for the investigation of the lecithin biomolecule. It was proven that the xenon atoms are absorbed between lecithin molecules and that they are sensitive to the heterogeneity of local motions of the fatty acid chains.

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2 Morphology and motional heterogeneity in styrene - methyl methacrylate diblock copolymers by ^1H and ^{13}C solid-state NMR

2.1 Introduction

Classical and advanced solid-state NMR methods were successfully applied to investigate a broad range of polymers with important applications such as diblock copolymers, confined lipids, biomaterials and biological tissues. An understanding of their microstructure and dynamics is necessary in order to manufacture materials with improved macroscopic properties.

Block copolymers have received much attention due to their unique chemical structures, which results in new physical and thermodynamic properties, that can be correlated to their solid-state and solution morphologies [Nos1, Haz1, Fas1, Par1, Ric1]. These block copolymers can be synthesized in various ways such as anionic [Att1], cationic [Gob1], Atom Transfer Radical Polymerization (ATRP) [Pin1] and coordination polymerization [Coa1]. ATRP is advantageous over all the other synthetic methodologies in synthesizing polymers with controlled architectures. Transition-metal-mediated living ATRP has been used successfully to achieve novel functional polymeric materials with new properties that are directly associated with the precise control of polymer architecture and the predetermined polymer molecular weight and molecular weight distribution (PDI). ATRP is tolerant to many impurities and functional groups, which is useful for it to be used in synthesizing many functional macromolecules [Pat1, Coe1, Saw1, Saw2, Mat1, Gro1].

Depending on the nature and length of each homopolymer sequence, block copolymers can be beneficial in providing wide range of materials with tailored properties. One of the most important applications of block copolymers at the industrial scale is their use as surfactants for the pharmaceutical, oil, agriculture, and detergent industries [Ham1]. They also found significant practical applications as adhesives [Mic1], sealants [Kat1], crosslinking agents for elastomers [Tho1], surface modifiers for fillers [Bal1], additives for resin gelefication and hardening [Wri1] and also as compatibilizing agents for emulsion polymerization [Jon1].

The diblock copolymers have a morphology consisting of mobile, interface and rigid regions, which are difficult to characterize by classical techniques like X-ray, SEM, DSC etc. The values of their domain sizes as well as their spatial distributions directly influence the macroscopic properties of the polymer therefore an investigation of them is necessary. Spin-diffusion NMR [Sch1 and references therein], employing different types of dipolar filters which select in separate experiments the magnetization coming from different regions, was employed to estimate the domain sizes of the mobile, interface and rigid components [Gol1, Cla1, Van1, Van2, Che1, Dem1, Dem2, Dem3, Dem4, Dem5, Dem6, Dem7]. Clauss *et al.* investigated by spin-diffusion NMR well-defined symmetrical diblock copolymers of poly(styrene) and poly(methyl methacrylate), PS-*b*-PMMA [Cla1]. The scaling dependence of the domain size on the block length was reported. Proton spin-diffusion experiments were also reported on poly(ethylene oxide)-*block*-poly(styrene) and poly(ethylene oxide)-*block*-poly(hydroxyethylmethacrylate) diblock copolymers [Dem3].

Recently, Tekely and coworkers discussed the motional heterogeneity of a series of poly(ether-*block*-amide) samples exploiting an approach based on the cross-polarization transfer efficiency combined with different well-established methods of high-resolution solid-state ^{13}C NMR spectroscopy [Huc1]. Subtle NMR spectroscopic fingerprints of the dynamic heterogeneity of the soft component of the poly(ether-*block*-amide) copolymer can be observed by indirect ^1H transverse magnetization relaxation measurements at different ^{13}C - ^1H cross-polarization contact times.

The aim of present work is to establish a phenomenological correlation between the mesoscopic and microscopic parameters of a series of styrene-*co*-methyl methacrylate (PS-*co*-PMMA) diblock samples. The mesoscopic parameters are given by the domain thicknesses of different phases measured by ^1H spin-diffusion NMR with a double-quantum dipolar filter. The heterogeneity at the microscopic level is investigated by ^1H second van Vleck residual moments $\langle M_2 \rangle$ edited from the PS diblock component by DQ build-up curves and high-resolution ^{13}C longitudinal magnetization relaxation in the rotating frame ($T_{1\rho}^C$). The revealed correlations and fingerprints of the heterogeneity of the chain motion are useful for a better understanding of the mechanical properties of diblock copolymers.

2.2 Experimental

Samples. Styrene (Sty, 98%, Merck) and methyl methacrylate (MMA, 98%, Merck) were vacuum distilled and kept below 5 °C before use. Methyl 2-bromopropionate (MBP, 99%, Aldrich), benzyl chloride (99%, CDH), 2, 2'-bipyridine (bpy, 99%, Lancaster), N, N, N', N'', N'''- pentamethylenetriamine (PMDETA, 99%, Aldrich) were used as received. Toulene (99%, Merck) was vacuum distilled before use.

PS-*b*-PMMA diblock copolymers were prepared by Sonia Gandhi at ITMC RWTH-Aachen by Atom Transfer Radical Polymerization (ATRP) [Nos1, Haz1, Fas1, Par1]. The macroinitiator of styrene (PSty-Br) was prepared by adding calculated amounts of styrene (S) monomer, PMDETA (ligand) and copper bromide (CuBr) in to a round bottom flask. The reaction mixture was kept in an ice bath and was degassed using three vacuum-nitrogen cycles for 5-10 minutes. A calculated amount of benzyl chloride (initiator) was the added to the reaction flask and again nitrogen was purged for 5-10 minutes. The flask was sealed and the polymerization was carried out in an oil bath maintained at 60 °C. The reaction mixture was taken out at different time intervals to monitor the progress of the polymerization. After completion of the polymerization, the reaction mixture was dissolved in a minimum amount of tetrahydrofuran (THF) and passed through a neutral alumina column to remove the catalyst. The resultant solution was reduced in volume by rotary evaporation of the excess THF. Precipitation of polymer was carried out in excess methanol. The polymer obtained was then vacuum dried and monomer conversion was determined gravimetrically.

This macroinitiator of desired molecular weight obtained was further used to synthesize the diblock copolymer. A calculated amount of PSty-Br macroinitiator was deposited in a round bottom flask and dissolved in a minimum amount of toluene. A calculated amount of PMDETA (ligand) and CuBr was added to the flask and the reaction mixture was degassed using three-vacuum nitrogen cycles. To this, a calculated amount of methyl methacrylate (MMA) monomer was added and again the system was degassed using three-vacuum nitrogen cycles. The flask was sealed and placed in an oil bath maintained at 60 °C. Withdrawing the samples at different time intervals, monitored progress of the polymerization. After completion of the polymerization, solution was passed through an alumina column, precipitated in water: methanol (1:1) mixture, polymer obtained was vacuum dried and the percentage conversion was measured gravimetrically. The molar mass M_n of all samples of the PS-*b*-PMMA diblock copolymer series is in the range of $(1.2 - 6.6) \times 10^4$ g/mol.

Proton NMR spin-diffusion experiments. The spin-diffusion experiments, using a double-quantum (DQ) dipolar filter, were performed in order to determine the thickness of the rigid, interfacial, and soft domains of the PS-*b*-PMMA diblock copolymers. In the present work ^1H spin-diffusion data were recorded at 500.44 MHz using a Bruker DSX 500 NMR spectrometer. The spin-diffusion experiments were performed with the pulse sequence $90^\circ_x - \tau - 90^\circ_{-x} - t_{\text{DQ}} - 90^\circ_y - \tau - 90^\circ_{-y} - t_d - 90^\circ_x - \text{FID}$ using an excitation/reconversion time τ of 7 μs and a variable spin-diffusion time t_d (Fig. 2.1). The evolution time of the DQ coherences (t_{DQ}) was 5 μs in all experiments. The length of 90° radio-frequency pulses was 3 μs and recycle delay was 3s. The spin-diffusion decay and buildup curves were analyzed using the model of one-dimensional lamellar morphology with three domains as described elsewhere [Dem3]. The spin-diffusion data were not corrected for the effect of longitudinal relaxation T_1 because, the spin-diffusion process was nearly completed at a mixing time of 25 ms. This time is significantly shorter than ^1H T_1 for all studied samples.

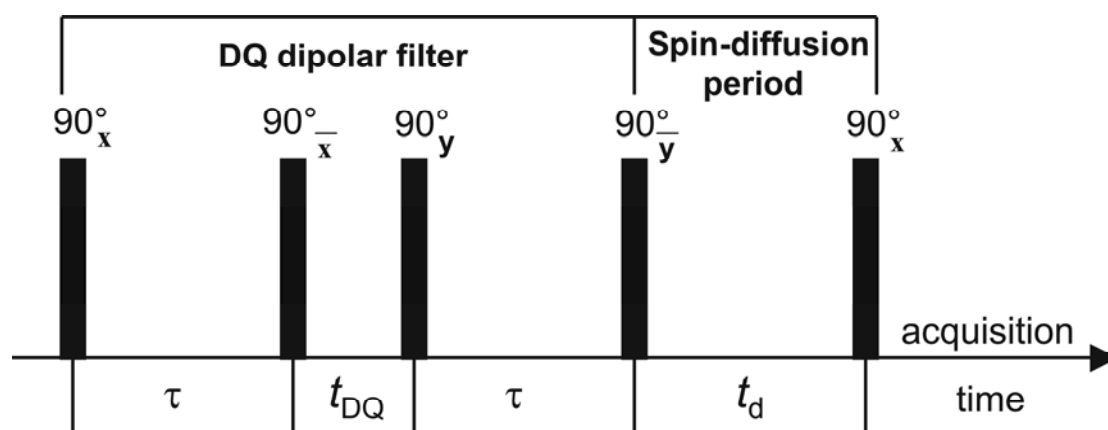


Fig. 2.1 Pulse-sequence for the spin-diffusion experiment with a double-quantum (DQ) filter. The first two pulses excite DQ coherences that evolve for a short time t_{DQ} . These coherences are converted by the following two pulses into z-magnetization. The spin-diffusion takes place during the time interval of duration t_d . The last pulse reads out the distribution of magnetization between different polymer fractions.

Proton double-quantum (DQ) build-up curves. The ^1H DQ build-up curves of PS-*b*-PMMA diblock copolymers were recorded using the five-pulse sequence shown in Fig. 2.1 [Dem8]. The excitation/reconversion times were varied in the range of 2-100 μs with a fixed spin-diffusion time of 10 μs . The maximum of the curve appears at a very short excitation time τ , in the range 5-10 μs indicating the presence of strong ^1H dipolar interactions. From the initial part of the DQ build-up curves, ^1H second van Vleck moment of the rigid domains of PS can be determined [Dem8].

Carbon-13 longitudinal magnetization relaxation in the rotating frame ($T_{1\rho}$). The solid-state ^{13}C cross-polarization magic angle spinning (CPMAS) NMR experiments were performed on a Bruker DSX 500 MHz spectrometer operating at 125.84 and 500.44 MHz for ^{13}C and ^1H , respectively. The pulse sequence used in ^{13}C $T_{1\rho}$ measurements is depicted in Fig. 1.5. The samples were placed as powder in a 4 mm CPMAS probe. The magic angle-spinning rate was set to 7.5 kHz to minimize spinning sideband overlap. The 90° pulse length for ^{13}C was $8.5\ \mu\text{s}$ and the decay of the ^{13}C magnetization in the spin-lock field was observed for spin-lock times of up to 40 ms.

2.3 Results and discussion

2.3.1 Second van Vleck moments by DQ build-up curves.

Proton second van Vleck moments $\langle M_2 \rangle$ give a measure of intra- and inter-chain dipolar couplings. The higher the value of $\langle M_2 \rangle$, the larger the dipolar couplings showing the chain motion hindrance, more perfect crystalline ordering, and denser packing.

Normalized DQ build-up curves are shown in Fig. 2.2a for PS-*b*-PMMA diblock copolymers with different number average molar masses. The maxima are found for excitation/reconversion times of around $12\ \mu\text{s}$ and correspond to the rigid part of the diblock copolymer of PS. The mobile PMMA component is not edited by the DQ filter.

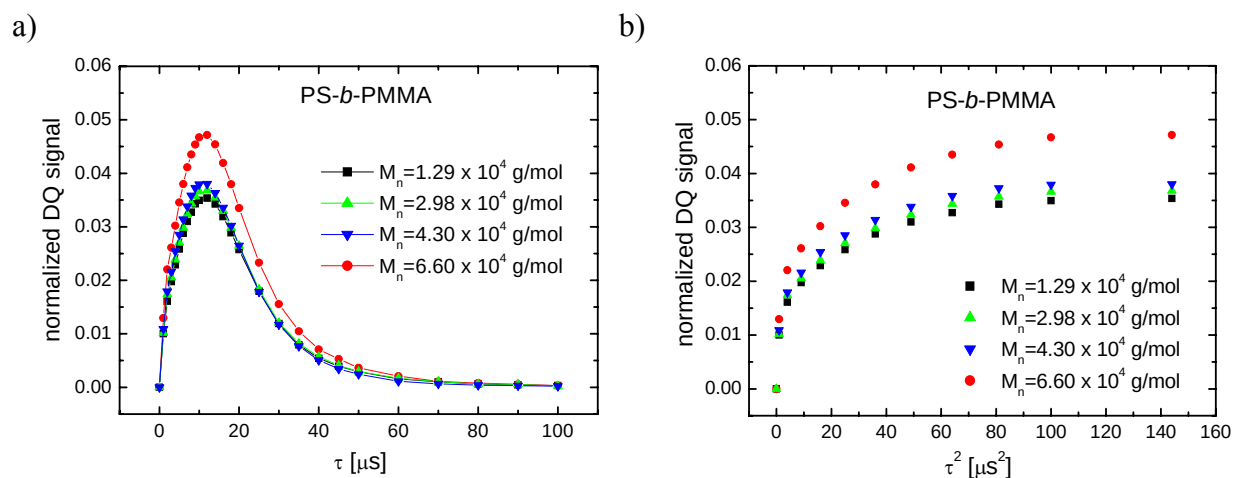


Fig. 2.2 (a) Proton DQ buildup curves for PS-*b*-PMMA samples with different molecular weights M_n . The maxima correspond to the residual dipolar couplings of the rigid phase. The excitation/reconversion time $\tau = 7\ \mu\text{s}$ is used for the DQ filter. (b) Initial part of the double-quantum buildup curve versus τ^2 .

The initial parts of the curves as a function of τ^2 are shown in Fig. 2.3b. It is evident that the initial slopes increase with the molar mass M_n of the diblock copolymer. Using the procedure discussed in Ref. [Dem8], the initial part of DQ build-up curve was fitted with a polynomial in τ^2 , where the first coefficient is proportional to the ^1H residual van Vleck moment $\langle M_2 \rangle$. Figure 2.3 indicates that $\langle M_2 \rangle$ increases with increasing molecular weight of PS-*b*-PMMA showing an increase of dipolar couplings inside of PS block which in turn shows an increase in the rigid component and higher order in the block copolymer.

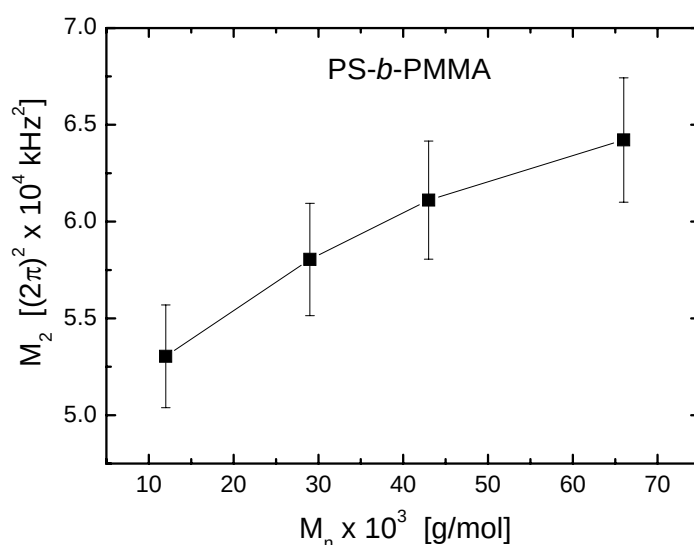


Fig. 2.3 The dependence of ^1H residual second van Vleck moments $\langle M_2 \rangle$ of the rigid fraction on the molecular weight of PS-*b*-PMMA.

2.3.2 Domain sizes of PS-*b*-PMMA diblock copolymers by ^1H spin-diffusion NMR with a DQ dipolar filter

A proton NMR spectrum of PS-*b*-PMMA with $M_n = 4.3 \times 10^4$ g/mol is shown in Fig. 2.4. For each diblock copolymer the NMR spectrum shows narrow, broad and intermediate components. The experimental wide-line spectra were decomposed into three components using the DMFIT program [Mas1]. The proton spectra of each sample were decomposed in terms of a Gaussian (rigid), intermediate (interface) and a Lorentzian (mobile) line.

In order to assign the components to the corresponding block, a proton spectrum of pure PS (not shown) with the same molecular weight as the PS block in the copolymer was recorded. Taking into account that no crystalline phase of PMMA is present in the

copolymers, the comparison of this spectrum with the proton spectra of the two copolymers indicates that the narrow peak is due to the mobile PMMA component. Thus the broad component is due to the PS block in PS-*b*-PMMA.

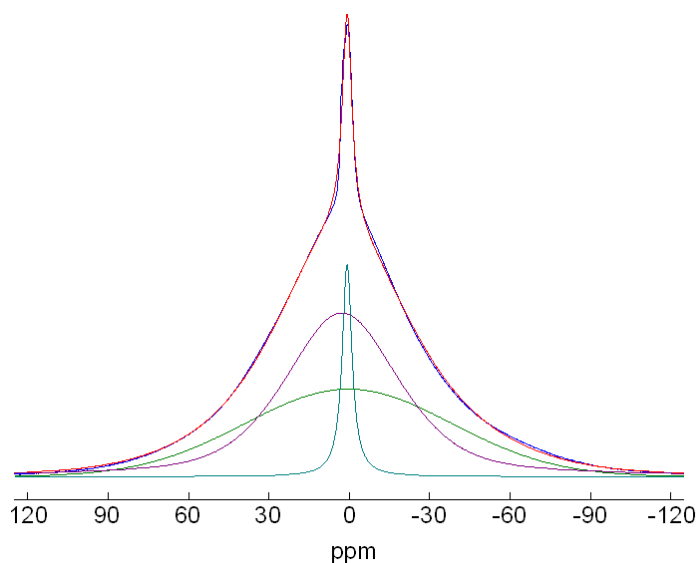


Fig. 2.4 Proton NMR spectrum of PS-*b*-PMMA decomposed into three components. The broad and narrow lines correspond to the rigid and mobile components and the intermediate line corresponds to the interface.

Double-quantum dipolar filter. The efficiency of the DQ dipolar filter is demonstrated in Fig. 2.5 for PS-*b*-PMMA with $M_n = 43000$ g/mol. The figure shows ^1H wide-line NMR spectra recorded with the DQ filter at different excitation/reconversion times τ (Fig. 2.1). For small τ values, the DQ filter edits only the signal of the rigid component (PS) with the strongest dipolar interactions. The ^1H -edited spectrum has the form of a doublet (Fig. 2.5a). The broadening of the DQ edited doublet is mainly due to the intergroup interactions in the rigid component. Thus, the magnetization corresponding mainly to the rigid fraction of the block copolymer is selected at short excitation times (5-10 μs). The resolution of the DQ edited doublet is reduced as the excitation/reconversion time increases, due to the increase in the size of the proton dipolar network (Fig. 2.5b). At long excitation times the DQ filter selects only the signal from the mobile component (Fig. 2.5c). This is attributed to the fact that the single-quantum coherences from the rigid and interface regions decay nearly to zero during the free evolution periods in the five-pulse sequence (Fig. 2.1). Thus, the DQ filter shows high efficiency in selecting the magnetization at a particular PS-*b*-PMMA domain with different molecular mobility. The use of this type of dipolar filter to select the rigid domains leads to a better evaluation of the integral intensities corresponding to different components due to more accurate detection of narrow signals on top of a broad component compared to the detection of a broad component under a narrow signal. The DQ edited spectra in combination with DQ

build-up curves allow us to choose the optimum filter time for selecting the magnetization of the rigid fraction. The value of $\tau = 7\mu\text{s}$ has been chosen, which still keeps the filter efficiency close to unity at reasonable value of the signal-to-noise ratio.

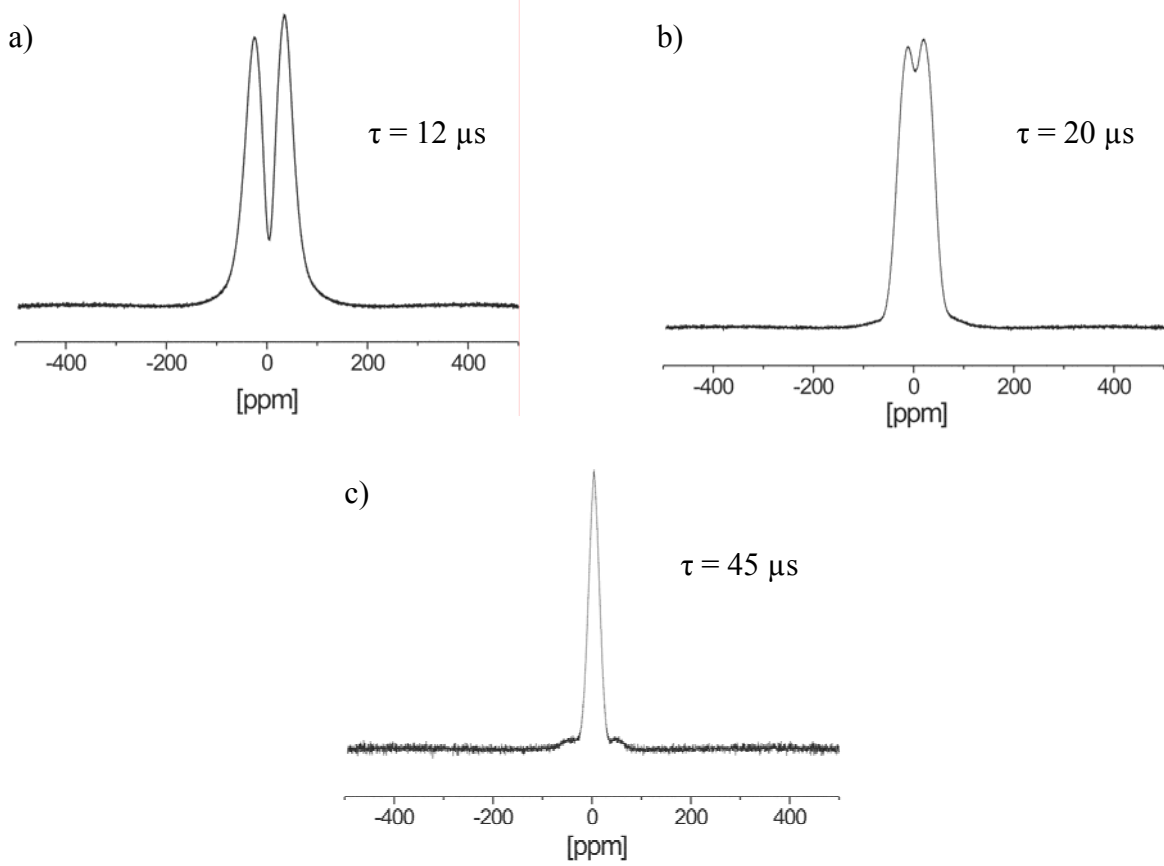


Fig. 2.5 Proton DQ filtered spectra for different excitation/reconversion times τ measured using the pulse sequence of Fig. 1 with $t_{\text{DQ}} = 5\mu\text{s}$ and $t_d = 10\mu\text{s}$. The spectra shown in (a) and (b) edit mainly the ^1H pairs of the hard segments. (c) For longer values of τ , the pulse sequence acts as a filter for the mobile component.

Proton spin diffusivities. The spin-diffusion coefficients have to be evaluated in order to estimate the domain sizes of the rigid, interface, and the mobile regions. Taking into account that the line shapes for the three spectral components are in a good approximation Gaussian, intermediate, and Lorentzian functions, the spin-diffusion coefficients can be evaluated [Dem1]. The spin-diffusion coefficients can be expressed in terms of the local dipolar field, so that the spin diffusivities are related to the second van Vleck moments [Dem6].

The equations used to calculate the spin-diffusion coefficients for rigid (Gaussian line), interface (intermediate line) and mobile (Lorentzian line) regions are given by [Dem1]

$$D_{\text{mobile}} \approx \frac{1}{6} \langle r^2 \rangle [\alpha \Delta v_{1/2}]^{1/2}, \quad (2.1a)$$

$$D_{\text{rigid}} \approx \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta v_{1/2}, \quad (2.1b)$$

$$D_{\text{interface}} \approx \frac{D_{\text{rigid}} + D_{\text{mobile}}}{2}, \quad (2.1c)$$

where α is the cutoff parameter of the Lorentzian line, $\Delta\nu_{1/2}$ is the full line width at the half-height, and $\langle r^2 \rangle$ is the mean-square distance between the nearest spins.

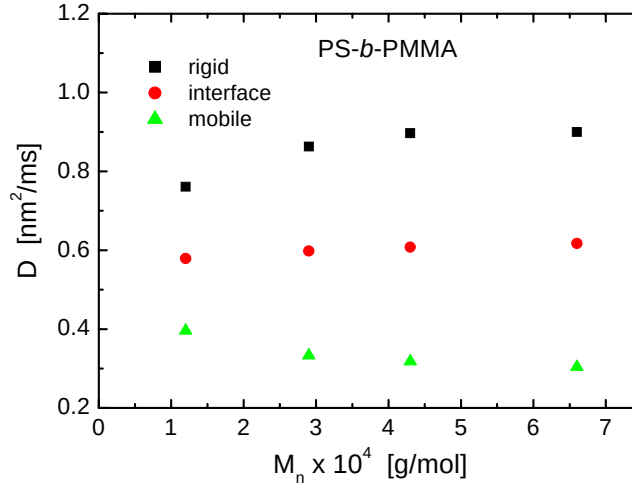


Fig. 2.6 Dependence of ^1H spin-diffusion coefficients of rigid, interface, and mobile component on the molecular weight of PS-*b*-PMMA diblock copolymers.

Taking into account the complexity of the chemical structure and the large number of protons in PS-*b*-PMMA, the $\langle r^2 \rangle$ values have been computed with molecular optimizations for both hard and soft segments by the Gaussian 03W software package (Gaussian Inc. Pittsburgh PA, 2003). The averaged $\langle r^2 \rangle^{1/2}$ values obtained for the hard (PS) and soft (PMMA) segment are 0.38 nm and 0.41 nm, respectively. Proton spin diffusivities of the rigid, interface, and mobile components were evaluated using the Eqs. 2.1 and the dependence on the molecular mass M_n is shown in Fig. 2.6. The results show that the strengths of the ^1H residual dipolar couplings increase in the regions of hard segment with an associated increase in the value of M_n .

Domain sizes. Proton spectra recorded after different diffusion times t_d (Fig. 2.1) using the DQ filter are shown in Fig. 2.7 for the PS-*b*-PMMA sample ($M_n = 4.3 \times 10^4$ g/mol). The source of z -magnetization was selected by the double-quantum filter mainly in the rigid region (PS). A decomposition of the proton spectra corresponding to different diffusion times was made into three components using the DMFIT program [Mas1]. For all PS-*b*-PMMA samples with different molecular weights, the equilibration of the magnetization takes place on a time scale smaller than the relaxation of the longitudinal magnetization; hence, a correction of the spin-diffusion data to account for relaxation effects has not been performed.

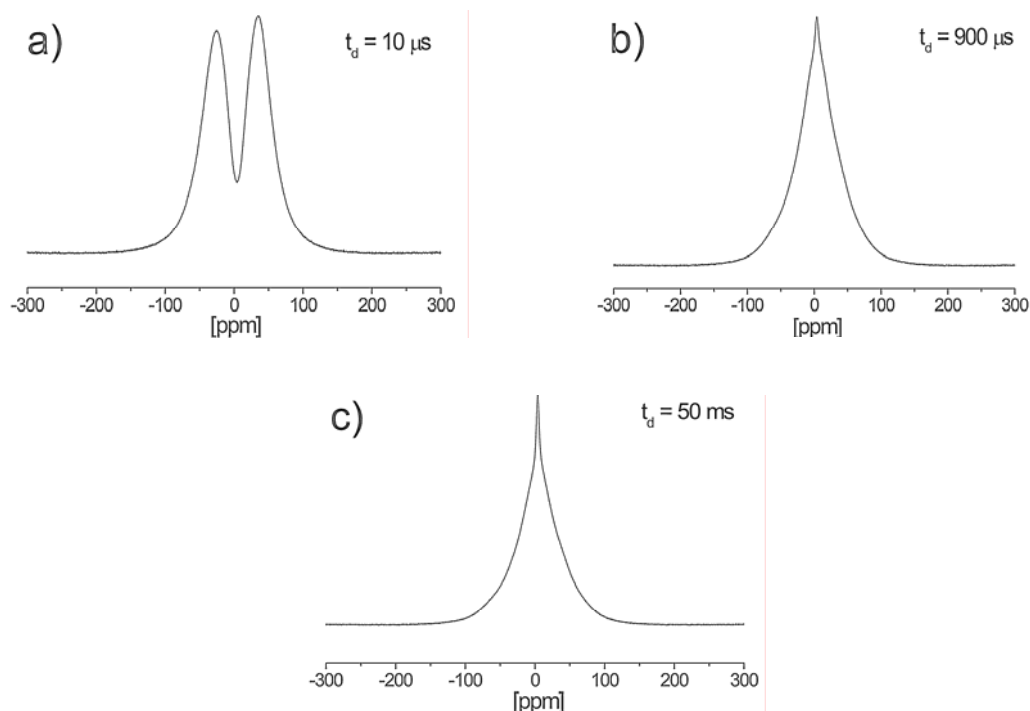


Fig. 2.7 Proton spin-diffusion edited NMR spectra at different diffusion times (a) $t_d = 10 \mu\text{s}$, (b) $t_d = 900 \mu\text{s}$, and (c) $t_d = 50 \text{ ms}$ for a PS-*b*-PMMA diblock copolymer ($M_n = 4.3 \times 10^4 \text{ g/mol}$).

The time-dependent integral spin-diffusion intensities obtained for the PS-*b*-PMMA sample ($M_n = 4.3 \times 10^4 \text{ g/mol}$) are shown in Fig. 2.8. It can be seen from this figure that a quasi-equilibrium is reached at about $t_d^{1/2} = 4.0 \text{ ms}^{1/2}$.

For a quantitative estimation of the domain sizes of the three phases, a fit of the decay and build-up curves has to be done by taking into account the plausible morphology of PS-*b*-PMMA to be lamellar. The curves obtained by the spin-diffusion experiments were fitted by calculating the integral intensities corresponding to each domain and using an analytical solution of spin-diffusion equations [Dem3]. This program assumes a one-dimensional morphology represented by three different domains with arbitrary sizes, diffusivities and proton densities, and the nuclear magnetization transfer occurs from a source and flows into a finite sink via an interface. Input values are the proton density, and diffusion coefficients. The values for the proton densities were estimated from the molecular density. They are $\rho_{\text{PS}} = 0.07 \text{ g/cm}^3$, $\rho_{\text{PMMA}} = 0.075 \text{ g/cm}^3$ and $\rho_{\text{interface}} = 0.0725 \text{ g/cm}^3$. The values for the diffusion coefficients were calculated as reported above (Fig. 2.6). The proton density and the diffusion coefficient corresponding to the interface have been taken as the arithmetic average of the corresponding values of PS and PMMA. Figure 2.8 reveals that the experimental data fit well with the simulations (solid lines) based on the analytical solutions for three-domain system with lamellar morphology.

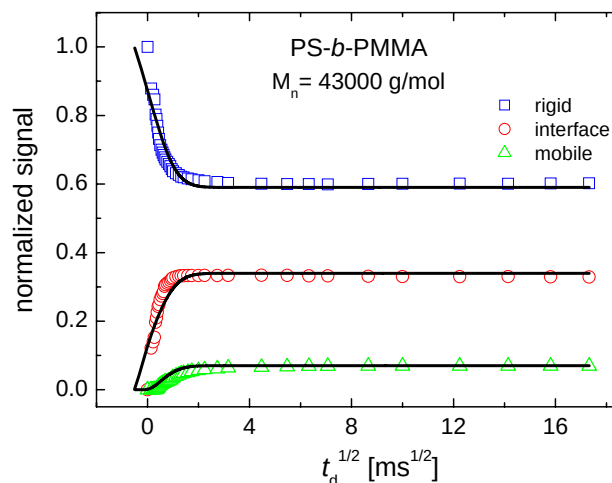


Fig. 2.8 Proton spin-diffusion decay and build-up curves as a function of $t_d^{1/2}$ for the three components (rigid, interface and mobile) for a PS-*b*-PMMA diblock copolymer ($M_n = 4.3 \times 10^4$ g/mol). The solid lines represent the simulations based on a 1D morphology.

Figure 2.9 shows the change in domain sizes of rigid, interface and mobile components of PS-*b*-PMMA with different molecular weights. The domain sizes of PS and the interface increase with molecular weight whereas the domain sizes of the mobile component decreases with molecular weight. To further verify the reliability of the NMR measurements of the microdomain structure, the dependence of the long period $d_{\text{long}} = d_{\text{PS}} + 2d_{\text{interface}} + d_{\text{PMMA}}$ on the molecular weights was plotted. In the case of a lamellar morphology theoretical studies predict that the molecular weight dependence of the lamellar spacing is given by a power law as $d_{\text{long}} \propto M^\alpha$, where the exponent α is 2/3 in the strong segregation limit and 1/2 in weak segregation limit [Nos1, Cla1].

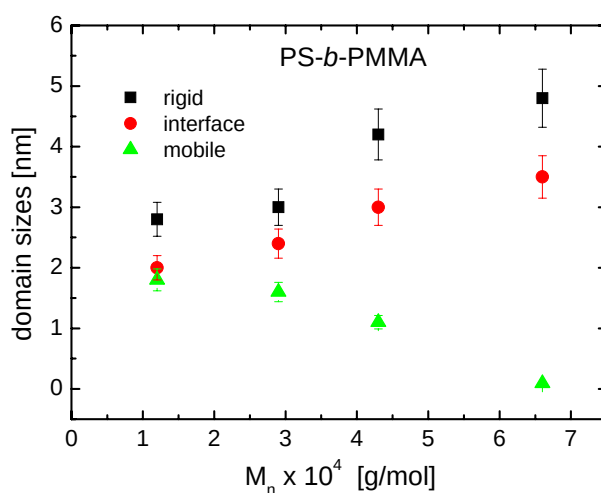


Fig. 2.9 Effective domain sizes for rigid, interface, and mobile phases as a function of M_n for PS-*b*-PMMA diblock copolymers.

The result depicted in Figure 2.10 in a double-logarithmic scale indicates good agreement with the two-thirds power law theoretically predicted in the strong segregation limit. Figure 2.10 shows a linear dependence of $\ln(d_{\text{long}})$ on $\ln(M_n)$ and the value of α obtained from the slope is 0.61, which lies in the strong segregation limit.

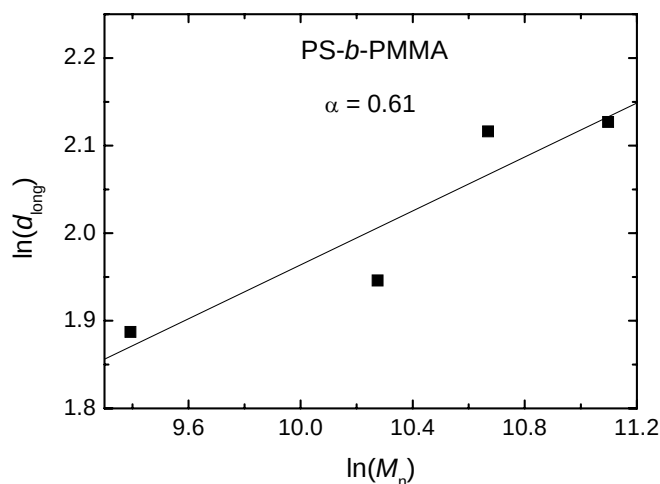


Fig. 2.10 Dependence of the long period of PS-*b*-PMMA block copolymers on the molecular weight on a double-logarithmic scale. The parameter α is the exponent of the scaling law.

2.3.3 ^{13}C longitudinal magnetization relaxation in the rotating frame

^{13}C NMR is a powerful technique for studying the local dynamics of diblock copolymers. The ^{13}C spin-lattice relaxation time in rotating frame is the important experimental quantity for probing the chain dynamics of different phases [Sch1]. Since the ^{13}C nucleus is of low natural abundance, the relaxation is dominated by the dipolar interactions with the directly bonded hydrogens and the ^{13}C chemical shielding anisotropy.

The heterogeneity of the polymer phase dynamics is affected by the molecular architecture and chemical composition of block copolymers. The bulk morphology of PS-*b*-PMMA cannot be revealed clearly by differential scanning calorimetry (DSC) and transmission electron microscopy (TEM) methods because the T_g values of PMMA (105° C) and PS (110° C) are close and their electron densities are too similar to ensure sufficient contrast. Thus, NMR is the most efficient method for PS-*b*-PMMA microphase characterization. Moreover, to the best of our knowledge, ^{13}C $T_{1\rho}$ measurements for PS-*b*-PMMA copolymers synthesized by ATRP have not been studied so far.

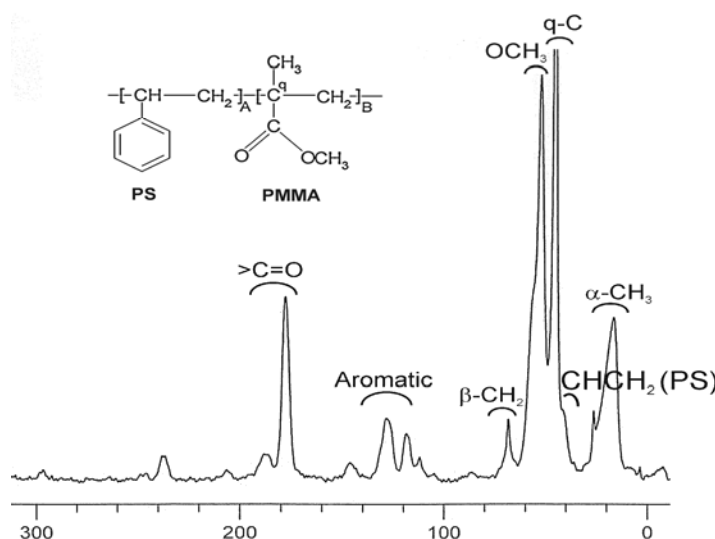


Fig. 2.11 CP-MAS ^{13}C spectrum of PS-*b*-PMMA with $M_n = 4.3 \times 10^4$ g/mol.

Figure 2.11 shows the completely assigned solid-state CP-MAS NMR spectrum of PS-*b*-PMMA ($M_n = 4.3 \times 10^4$ g/mol) at room temperature. The signals centered at $\delta = 178$ ppm, $\delta = 69.0$ ppm, $\delta = 58.1$ ppm, $\delta = 47.0$ ppm, $\delta = 41.0$ ppm and $\delta = 20.0$ ppm have been assigned to carbonyl (PMMA), β -methylene (PMMA), methoxy (PMMA), quaternary carbon (PMMA), CHCH_2 (PS), and α -methyl, respectively. The signals of aromatic carbons are split as a result of the different environment of the carbons.

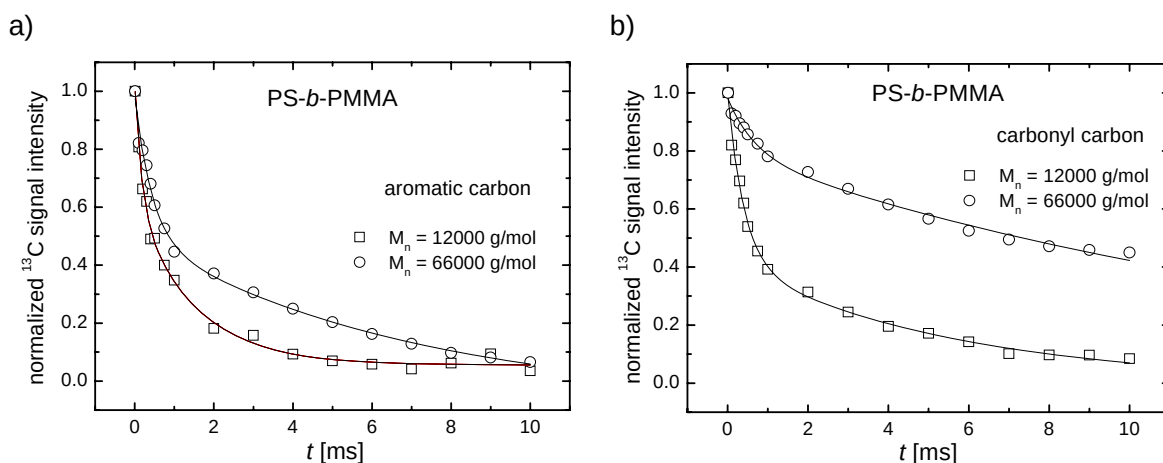


Fig. 2.12 Longitudinal magnetization decays in the rotating frame experiment (Fig. 2.2) of ^{13}C normalized signals of the a) aromatic and b) carbonyl groups. The $T_{1\rho}$ decays are shown for two different molecular weights of the PS-*b*-PMMA block copolymer. The solid lines are the biexponential fits of the data.

Carbon-13 longitudinal magnetization relaxation time in the rotating frame, $T_{1\rho}$, for the aromatic carbons (PS) and carbonyl carbon (PMMA) of the PS-*b*-PMMA was measured using the pulse scheme described in Fig. 1.5, with variable spin-locks on the carbon channel

following the initial cross-polarization sequence. By means of the cross-polarization transfer from adjacent protons, the ^{13}C magnetization was generated. Then, under high power proton decoupling, the high resolution ^{13}C signals were recorded and Fourier transformed. Selectively calculating the integrals of the peaks corresponding to the ^{13}C nuclei of interest, the $T_{1\rho}$ relaxation time values were finally obtained by fitting the decaying curves acquired as a function of spin-lock pulse length for each individual ^{13}C spin.

Figure 2.12 shows the experimental data obtained from ^{13}C $T_{1\rho}$ measurements for aromatic and carbonyl carbons which were fitted with a biexponential function given by:

$$S(t) = A_{\text{short}} \exp(-t/T_{1\rho}^{\text{short}}) + A_{\text{long}} \exp(-t/T_{1\rho}^{\text{long}}), \quad (2.2)$$

where A_{short} and A_{long} are the relative amplitudes for fast and slow components ($A_{\text{short}} + A_{\text{long}} = 1$), respectively. The transport constants $T_{1\rho}^{\text{short}}$ and $T_{1\rho}^{\text{long}}$ are the ^{13}C spin-lattice relaxation times in the rotating frame for the fast and slow components, respectively. The experimental data fitted well with the biexponential decay function, as shown in Figure 2.12a and b, which confirms the presence of a rigid and a less rigid phase in the PS component, by two different relaxation times corresponding to fast and slow decay. The PMMA component also shows the presence of a mobile and less mobile phase showing two different relaxation decays (Fig. 2.13). Hence the plausible morphology comprises of three phases, i.e., rigid (PS), mobile (PMMA) components and an interface, where the interface comprises one part from PS and one from PMMA.

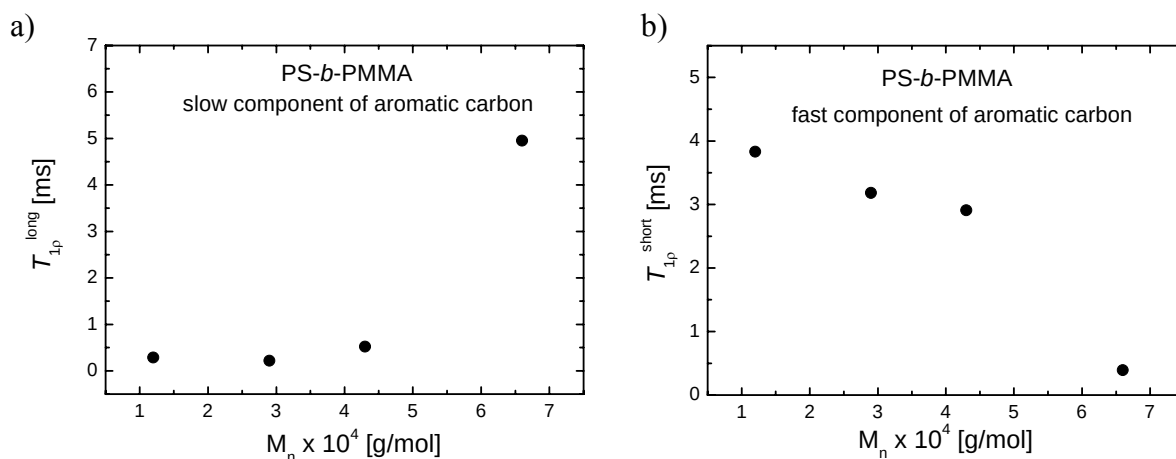


Fig. 2.13 Dependence of the a) long and b) short ^{13}C $T_{1\rho}$ relaxation time of the aromatic carbon of PS on the diblock copolymer molecular weight.

Figure 2.13a shows the plot of $T_{1\rho}^{\text{long}}$ originating from the more rigid phase of PS as a function of the molecular weight. The phenyl motion is more hindered and hence ^{13}C $T_{1\rho}^{\text{long}}$

increases as M_n becomes larger due to an increase in the chain packing and order. The interfacial fraction of the PS-*b*-PMMA contains less rigid PS chains. Its ^{13}C longitudinal relaxation time in the rotating frame corresponds to $T_{1\rho}^{\text{short}}$. From Fig. 2.13b it can be seen that $T_{1\rho}^{\text{short}}$ decreases with increasing molecular weight. The larger value of the free volume of the interfacial domain, which increases with molecular weight, leads to smaller values of $T_{1\rho}^{\text{short}}$.

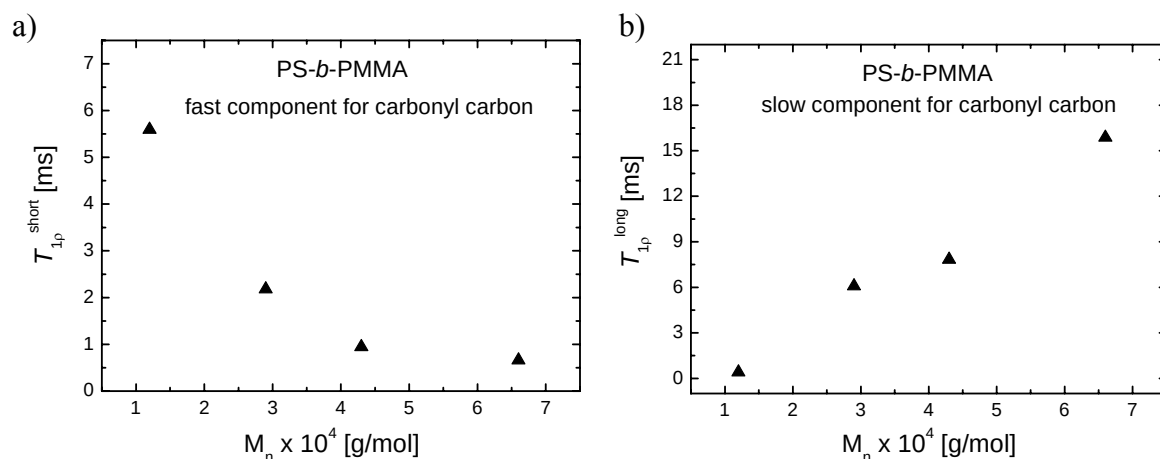


Fig. 2.14 Dependence of the a) short and b) long ^{13}C $T_{1\rho}$ relaxation time of the carbonyl carbon of PMMA on the diblock copolymer molecular weight.

The dependence of the ^{13}C longitudinal relaxation time in the rotating frame for the carbonyl carbon belonging to the PMMA copolymer as a function of M_n is shown in Fig. 2.14. For larger values of M_n , the PMMA chains move with larger amplitudes and shorter correlation times, and therefore, $T_{1\rho}^{\text{long}}$ increases (Fig. 2.14b). The opposite effect prevails in the interfacial region (Fig. 2.14a).

2.4 Conclusions

The morphology of PS-*b*-PMMA block copolymers was quantitatively characterized by mesoscopic parameters corresponding to the domain thicknesses. The sizes of rigid, interface and mobile components were estimated based on a general analytical solution of the spin-diffusion equation in a lamellar morphology composed of three domains. These results were obtained by exploiting the molecular weight dependence of the ^1H spin-diffusivities for the different phases. The correlation of the long period on the block copolymer with the

molecular weight of the diblock copolymer indicates good agreement with the theoretical prediction $d_{\text{long}} \propto (M_n)^{2/3}$.

The microscopic properties of the diblock copolymer phases were investigated by measurements of ^1H residual van Vleck moment ($\langle M_2 \rangle$) of the rigid PS component and by high-resolution ^{13}C $T_{1\rho}$ relaxation. In the former case an increase in M_n induces larger values of $\langle M_2 \rangle$ due to increase in the chain packing and orientation. Therefore, this microscopic parameter that reflects the strength of the dipolar couplings correlates with the domain sizes.

The high-resolution ^{13}C $T_{1\rho}$ relaxation time shows that the interfacial region contains components from PS and PMMA. The motional chain heterogeneity in the interface and in each component of the diblock copolymer is a function of the molecular weight. Therefore, the heterogeneity of the chain motion can be correlated with $\langle M_2 \rangle$ and the domain sizes. Understanding the interplay between microscopic and mesoscopic properties of diblock copolymer is helpful for a better assessment of the role of the morphology in determining the mechanical properties of these systems.

2.5 References

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3 Site-selective segmental dynamics by stimulated echo decay under rotor-synchronized MAS. Application to elastomers

3.1 Introduction

A technologically important class of materials is represented by elastomers [Bry1, Mar1, Eli1], which thus have been intensively investigated by various NMR techniques [Coh1], including 2D spectroscopy [Sot1, Dem1 and references therein]. From the NMR point of view, cross-linked elastomers exhibit both liquid-like and solid-like features. At temperatures well above the glass transition temperature, the time scales of molecular motions are liquid-like. However, the presence of topological constraints and permanent cross-links prevents the chain motion from being isotropic. Thus, anisotropic spin interactions, such as the dipole-dipole coupling, are not completely averaged out and give rise to solid-like properties [Dem3, Sot1, and references therein]. Depending on the degree of motional restriction, these residual dipolar couplings may be quite small, i.e., on the order of a few percent of those found in rigid solids [Dem3].

Residual dipolar interactions are reflected in different ways in the various NMR parameters. For instance, the short-time behavior of ^{13}C -edited transverse ^1H relaxation curve [Dem7] or of cross-polarization build-up curves [Dem8] is dominated by residual dipolar interactions within functional groups. Inter-group residual dipolar couplings (such as the CH-CH₂ coupling) on the other hand, can be investigated using 1D and 2D ^1H magnetization-exchange spectroscopy [Dem1]. Homonuclear and heteronuclear multiple-quantum NMR spectroscopy and build-up curves were used to measure residual dipolar couplings in different elastomers [Dem2, Dem3, Dem4, Dem5]. In all cases the measured residual dipolar couplings are found to be sensitive to the cross-link density and can be correlated with viscoelastic properties, such as the shear modulus.

The results obtained by a new NMR method allowing the measurements of the site-selective ^1H residual dipolar couplings by the stimulated echo decay under rotor-synchronized

MAS are discussed in this chapter. The method was tested on a series of natural rubber (NR) samples with different cross-link densities.

3.2 Experimental

The investigated elastomer samples are of commercially available natural rubber, i.e., SMR10 (Malaysia). The additives were 3 phr (*parts-per-hundred-rubber*) ZnO and 2 phr stearic acid. The sulfur and accelerator contents are given for the cross-link series of NR in Table 3.1. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-*tert*-butyl-sulfenamide). After mixing the compounds in a laboratory mixer at 50° C, the samples were vulcanized at 160° C in a Monsanto MDR-2000-E vulcameter. The degree of cross-linking was measured by the low frequency shear modulus or torque G (cf. Table 3.1) at a temperature of 160° C in the vulcameter directly after vulcanization. The measurements were performed with an oscillation amplitude of $\pm 0.5^\circ$ and a frequency of 1.67 Hz. The stress-strain curves were measured at room temperature at a strain velocity of 3 mm/min. The stress-strain curves ranged between 1-15% strain. The average values of the Young modulus E are reported in Table 3.1.

Table 3.1 Properties of the series of cross-linked NR samples

Sample	Sulfur-accelerator content (phr)	Shear modulus ^a G (dNm)	Young modulus ^a E (MPa)
NR1	1-1	5.2	0.9
NR2	2-2	8.5	1.5
NR3	3-3	11.2	2.0
NR4	4-4	13.2	2.1
NR5	5-5	14.5	2.2
NR6	6-6	15.4	2.4
NR7	7-7	16.2	2.8

^aThe uncertainties are less than 10 %.

Proton NMR wideline spectra, ^1H 2D NOESY and ^1H rotor synchronized stimulated-echo decay (ROSY-SED) measurements were done with a Bruker DSX 500 spectrometer. For all the measurements, 10 kHz magic angle spinning (MAS) was used. The length of the 90° pulse was 5.5 μs at a power attenuation of 6 dB. A 3 s recycle delay was used for the

conventional ^1H wideline spectra and 2D NOESY experiments. For the ROSY-SED experiment, whose scheme is presented in Fig. 3.1, a very short repetition time of 500 ms was used in combination with radio-frequency pulses of flip angle $\theta < 90^\circ$.

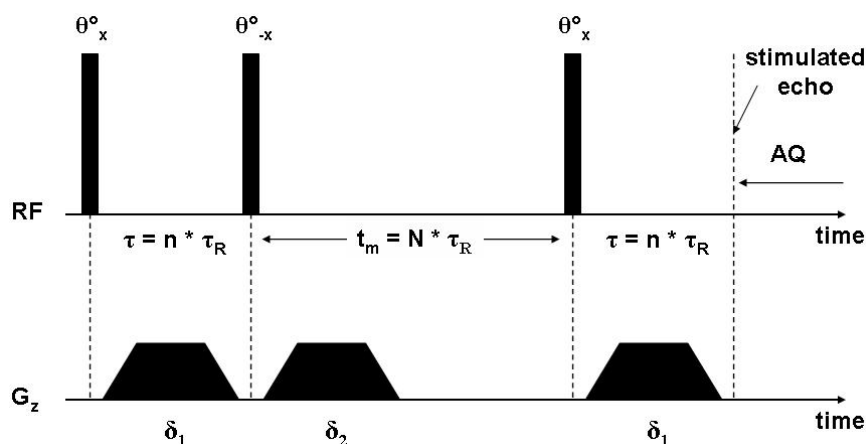


Fig. 3.1 Pulse sequence and scheme of the static magnetic field gradients used for detection of the stimulated echo decay under MAS. The radio-frequency pulses of flip angle θ together with a short recycle delay allow fast acquisition of echo decays. The time intervals τ and the mixing time t_m are rotor synchronized. The gradients G_z of duration δ_1 and δ_2 are used for coherence dephasing.

3.3 Theory

3.3.1 Spin-system model

The model that is considered for the evaluation of site-selective residual dipolar couplings by ROSY-SED is shortly discussed in the following. This model is adapted to natural rubber, which can be considered identical with 1,4-*cis*-polyisoprene.

(i) Depending on the time scale of the NMR experiment and its features, the existence of an extended proton dipolar network along the polymer chain can be proven. For instance, 2D ^1H magnetization-exchange NMR was used to investigate intergroup residual dipolar couplings in a cross-link series of poly(styrene-co-butadiene), (SBR) elastomers [Dem1]. The magnetization-exchange process between the CH and CH₂ group in the regime of short mixing time provides valuable insight regarding molecular order. Moreover, ^1H DQ MAS high-resolution spectra were recorded for SBR [Dem6] as well as NR [Dem4] by using recoupling pulse sequences with long excitation times. Similar to the NOESY spectra measured for static samples [Dem1], these DQ edited spectra directly showed the existence of

dipolar connectivities between all functional groups. Therefore, we expect cross-peaks between all functional groups of NR in NOESY/MAS experiments (see Fig. 3.3).

(ii) Many NMR experiments show the existence of a *strong hierarchy* of the dipolar couplings in elastomers. The dipolar couplings inside methylene groups are the most intense followed by those inside the methyl groups. The intergroup dipolar couplings can be estimated from the van Vleck second moment calculated for the rigid natural rubber [Gut1]. The intergroup and interchain contributions are about 30% of the intragroup second moment. At temperatures well above the glass transition temperatures, the interchain dipolar couplings are reduced even more and can be neglected in a good approximation. As a result of the strong hierarchy of the residual dipolar couplings only the dipolar couplings between neighboring functional groups along the polymer chains will be considered in the evaluation of the residual dipolar couplings.

(iii) The presence of the dangling chains and the polymer polydispersity is also neglected in this model.

3.3.2 Spin – pair residual dipolar Hamiltonian

A simple model to describe the NMR spin system response consists of a single polymer chain between two network junction points [Coh1]. The chain is considered to carry many NMR-active bonds. The spin-pair residual dipolar interactions can be evaluated by using the scale-invariant polymer model [Coh1]. In this model, the dipolar interactions are averaged over all conformations of an intercross-link chain subjected to the constraint that the end-to-end vector $\mathbf{R}$ is fixed. For such a chain, the residual dipolar coupling in the secular approximation of ij spin pairs may be expressed as [Sot1]

$$\overline{H}_d^{(ij)} = \left(-\sqrt{6}\right) \frac{k}{N^2 a^2} \mathbf{R}^2 P_2(\cos\beta) D^{(ij)} S^{(ij)} T_{2,0}^{(ij)}, \quad (3.1)$$

where the dipolar coupling constant is

$$D^{(ij)} = \left(\frac{\mu_0}{4\pi}\right) \frac{\gamma^2 \hbar}{r_{ij}^3}. \quad (3.2)$$

The internuclear distance is denoted by r_{ij} and the significance of the other quantities is given in Ref. [Dem6]. The bar in Eq. (3.1) represents the time average over the molecular reorientation process, which is faster than the spin-precession period in the local dipolar field of the rigid lattice. This averaging by rapid segmental motions is referred to as “pre-

averaging". The dynamic order parameter is given by $S^{(ij)} = \bar{P}_2[\cos\beta_{ij}(t)]$, where $\bar{P}_2$ is the pre-averaged second-order Legendre polynomial and $\beta_{ij}(t)$ is the instantaneous angle between a given $\mathbf{r}_{ij}$ internuclear vector and $\mathbf{R}$. Under pre-averaging condition, the angle β can be considered to define the direction of $\mathbf{R}$ with respect to the direction of the static magnetic field $\mathbf{B}_0$. The site-selective dynamic order parameter $S^{(ij)}$ takes into account the existence of the segmental dynamic heterogeneities along the polymer chain. A scaled dynamic order parameter can be defined as $S_s^{(ij)} = S^{(ij)} / N_e$, where the effective number of statistical segments is $N_e = N / k$. The number of statistical segments, each of the length a , of the polymer chain between two cross-link points is denoted by N . The geometrical factor k depends on the model adopted to describe the chain statistics [Sot1] and is equal to 3/5 for a chain of freely jointed segments. Finally, $T_{2,0}^{(ij)}$ is the irreducible tensor operator describing the spin part of the secular dipolar interaction of i and j spins [Bow1].

If the length of the statistical segment is denoted by a and the dimensionless squared end-to-end vector $\mathbf{q}^2 = \mathbf{R}^2 / Na^2$ is introduced in Eq. (3.1), we can write

$$\bar{H}_d^{(ij)} = (-\sqrt{6})\mathbf{q}^2 P_2(\cos\beta) D^{(ij)} S_s^{(ij)} T_{2,0}^{(ij)}, \quad (3.3)$$

In our NMR experiments on elastomers, the dipolar spin interactions are time modulated. Segmental motions produce a random modulation of the dipolar Hamiltonians. The sample rotation at the magic angle induces a coherent modulation at the frequencies $\omega_R / 2\pi$ and ω_R / π , where ω_R is the rotor pulsation. In the case of simultaneous presence of both segmental motions and magic angle spinning, from Eq. (3.3) we can write

$$\bar{H}_d^{(ij)}(\omega_R t) = (-\sqrt{6})\mathbf{q}^2 D^{(ij)} S_s^{(ij)} \left\{ -\frac{1}{\sqrt{2}} \sin[2\beta] \cos[\omega_R t + \gamma] + \frac{1}{2} \sin^2[\beta] \cos[2\omega_R t + 2\gamma] \right\} T_{2,0}^{(ij)}, \quad (3.4)$$

where the Euler angles (α, β, γ) describe the orientation of $\mathbf{R}$ in the rotating frame.

In the presence of segmental motions the Euler angles become random functions of time, i.e., $(\alpha(t), \beta(t), \gamma(t))$. Finally, the dipolar Hamiltonian modulated by both types of motions has the form

$$\begin{aligned} \bar{H}_d^{(ij)}(\omega_R t; t) = & (-\sqrt{6})\mathbf{q}^2 D^{(ij)} S_s^{ij} \cdot \\ & \cdot \left\{ -\frac{1}{\sqrt{2}} \sin[2\beta(t)] \cos[\omega_R t + \gamma(t)] + \frac{1}{2} \sin^2[\beta(t)] \cos[2\omega_R t + 2\gamma(t)] \right\} T_{2,0}^{(ij)}. \end{aligned} \quad (3.5)$$

3.3.3 Total spin Hamiltonian

The total spin Hamiltonian is considered to describe the intra- and inter-group residual proton interactions under the conditions of anisotropic motional pre-averaging by fast molecular motion. In the rotating frame representation, the time-dependent total Hamiltonian for a rotating sample is given by

$$H(t) = H_z + \sum_l \bar{H}_d^{(l)}(\omega_R t; t) + \sum_{l>m} \bar{H}_d^{(lm)}(\omega_R t; t), \quad (3.6)$$

where $l, m = CH, CH_2$, and CH_3 . The spin systems of methylene and methyl functional groups are equivalent with a fictitious spin $F = 1$ and $F = 3/2$ respectively [Dem5]. The chemical-shift anisotropy and heteronuclear couplings are neglected in Eq. (3.1). The Zeeman Hamiltonian is

$$H_z = \sum_l^{1,3} H_z^{(l)}, \quad (3.7)$$

where

$$H_z^{(l)} = -\Delta\Omega_l F_z^{(l)}. \quad (3.8)$$

The off-resonance pre-factors are $\Delta\Omega_l = (\omega_0 + \delta_l) - \omega = \Delta\omega + \delta_l$, where ω_0 is the Larmor pulsation, ω is the radio-frequency pulsation, and δ_l is the isotropic chemical shift. The total spin operator is the sum of the individual spin operators $I_{z,i}$ of each proton, i.e., $F_z^{(l)} = \sum_i^{1,n_l} I_{z,i}$, where $n_l = 1, 2$, and 3 for CH , CH_2 and CH_3 groups, respectively. When the resonance condition $\omega = \omega_0$ is fulfilled the total Zeeman Hamiltonian is

$$H_z = -\sum_l^{1,3} \delta_l F_z^{(l)}. \quad (3.9)$$

We note that the following commutations relationship are fulfilled, i.e.,

$$[F_z^{(l)}, \bar{H}_d^{(m)}(\omega_R t; t)] = 0, \quad (3.10)$$

$$[F_z^{(l)}, \bar{H}_d^{(lm)}(\omega_R t; t)] \neq 0. \quad (3.11)$$

for any l and m . Therefore, in the first approximation, the polarization exchange of each functional group is due only to intergroup dipolar couplings. Nevertheless, because

$$[\bar{H}_d^{(m)}(\omega_R t; t), \bar{H}_d^{(lm)}(\omega_R t; t)] \neq 0, \quad (3.12)$$

in the second approximation, the polarization of each functional group is affected also by the intragroup dipolar couplings via intergroup interactions.

The dipolar interactions fluctuate randomly around the residual dipolar couplings modulated coherently by the MAS. Therefore, the total Hamiltonian given by Eq. (3.6) can be rewritten as

$$H(t) = H_z + \sum_l \bar{\bar{H}}_d^{(l)}(\omega_R t) + \sum_{l>m} \bar{\bar{H}}_d^{(lm)}(\omega_R t) + \sum_l \Delta \bar{H}_d^{(l)}(\omega_R t; t) + \sum_l \Delta \bar{H}_d^{(lm)}(\omega_R t; t), \quad (3.13)$$

where the fluctuations of the secular dipolar Hamiltonians around the residual values are given by the Hamiltonians

$$\Delta \bar{H}_d^{(l)}(\omega_R t; t) \equiv \bar{H}_d^{(l)}(\omega_R t; t) - \bar{\bar{H}}_d^{(l)}(\omega_R t), \quad (3.14)$$

and

$$\Delta \bar{H}_d^{(lm)}(\omega_R t; t) \equiv \bar{H}_d^{(lm)}(\omega_R t; t) - \bar{\bar{H}}_d^{(lm)}(\omega_R t). \quad (3.15)$$

We shall note that the residual dipolar Hamiltonians $\bar{\bar{H}}_d^{(l)}(\omega_R t)$, and $\bar{\bar{H}}_d^{(lm)}(\omega_R t)$ are averaged to zero for a full rotor period. Each of the dipolar Hamiltonians discussed above depends on the end-to-end vector length and its Euler angles. Therefore, to describe the NMR response of a polymer network, averages over these quantities have to be performed.

The Hamiltonians in Eqs. (3.14) and (3.15) describe the spin-system response and the dependence on the cross-link density (C). The C quantity can be defined in different ways. One possibility is to use the number of Kuhn segments N , i.e., $C = 1/N$. It is evident from Eq. (3.5) that the total Hamiltonian should be proportional with $1/N = C$. It can be shown [Dem1] that in the initial time regime of the spin-system response, the trace of the square of total spin Hamiltonian is present. Therefore, the spin-system response in this initial time approximation depends on $(1/N)^2 = C^2$. In our NMR experiment the measured quantities are investigated as a function of cross-link density C .

3.4 Results and discussion

3.4.1 Proton MAS spectra

The fast MAS conditions can be easily fulfilled in elastomers. The values of the residual dipolar couplings (ν_D) are of the order of kHz and therefore, the experiments can be done under $\nu_R \gg \nu_D$, where ν_R is the sample spinning frequency.

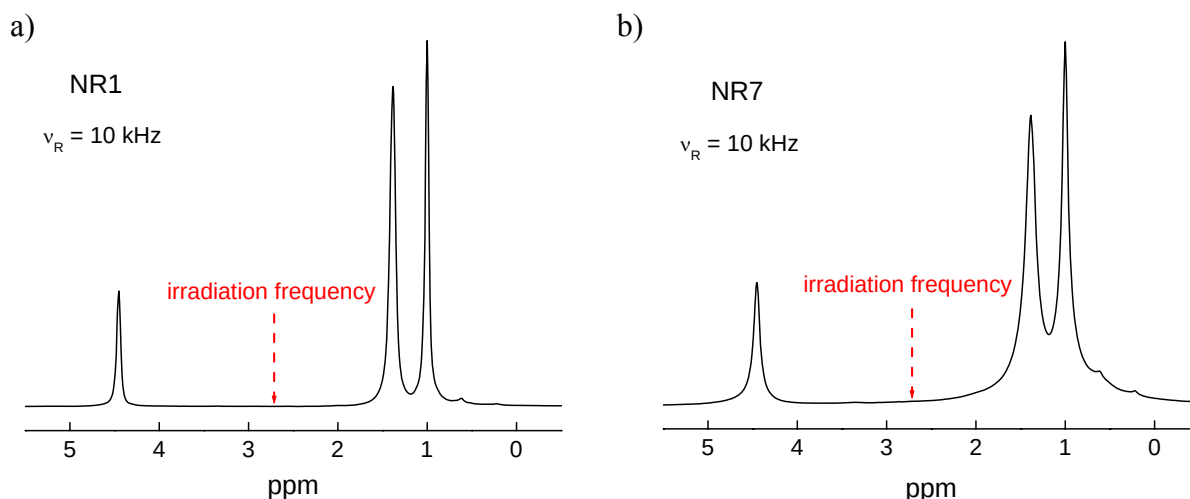


Fig. 3.2 Proton high-resolution spectra of cross-linked natural rubber (NR) samples NR1 and NR7 (Table 3.1) measured at 500 MHz 10 kHz MAS. The resonances correspond to the CH_3 , CH_2 , and CH functional groups (going downfield). The irradiation frequency is applied in the middle of each spectrum.

The proton spectra measured under fast MAS at ν_R for two relevant NR samples with the extreme values of the cross-link density are shown in Fig. 3.2. The spectral resolution is good and starts to deteriorate slightly at larger values of the cross-link density.

3.4.2 Proton NOESY spectra

The existence of the fluctuating ^1H dipolar couplings in cross-linked NR samples can be proven directly by the existence of high intensity cross-peaks in the NOESY 2D spectrum (Fig. 3.3). The cross-peaks are detected between all functional groups. The existence of slow segmental motions is indicated by the existence of the positive cross-peaks in Fig. 3.3.

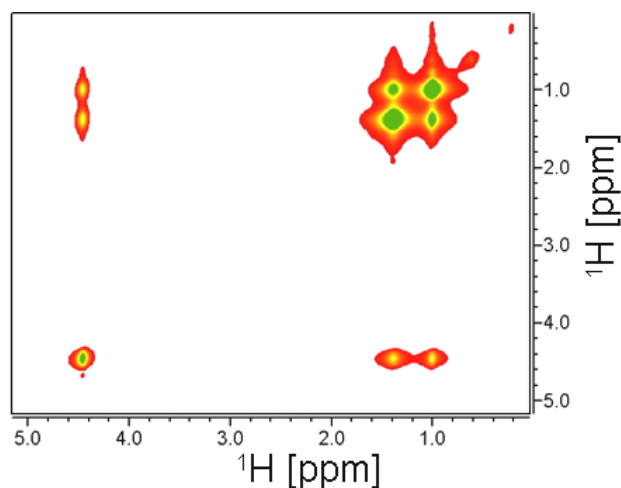


Fig. 3.3 Two-dimensional ^1H NOESY spectrum of NR1 under fast MAS at $\nu_R = 10 \text{ kHz}$.

3.4.3 ROSY-SED

The ROSY-SED method starts from the classical Ernst approach based on the use of small flip angles and short recycling delays. This method, combined with the detection of the NMR signals under MAS at high magnetic fields, allows a substantial reduction of the measurement time.

The scheme used for the ROSY-SED experiments is shown in Fig. 3.1. The method allows the characterization of segmental dynamics of soft solids, like elastomers, by measuring the stimulated echo decay of each functional group under fast MAS. An important feature of the experiment is the possibility to investigate slow segmental motions that can be further correlated with the mechanical properties. The long lifetime of the stimulated echo is responsible for this feature. For elastomer materials, ^1H residual dipolar couplings coexist with randomly fluctuating dipolar couplings. In order to make the stimulated echo decay sensitive only to the segmental motions, a rotor synchronization of the time intervals τ and the mixing time t_m is needed.

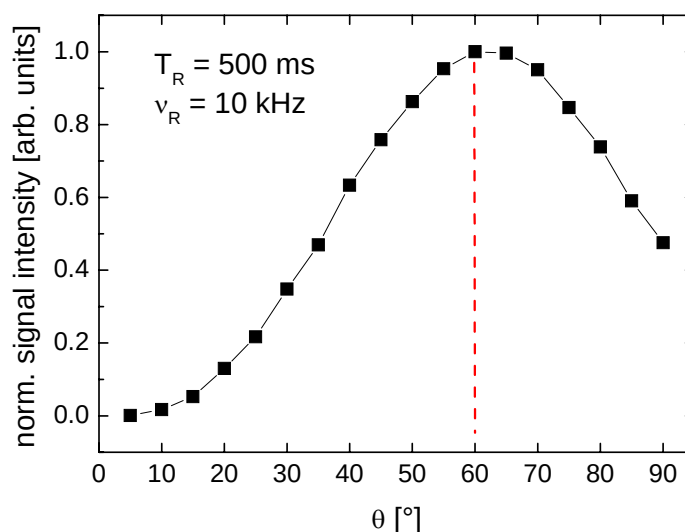


Fig. 3.4 The dependence of the ^1H total integral intensity of NMR spectrum of NR1 as a function of the pulse flip angle θ . The experiment was done under MAS at $\nu_R = 10$ kHz and for a fixed value of the recycle delay $T_R = 500$ ms.

The first step in applying the ROSY-SED experiment was to set the optimum value of the flip angle θ , for a fixed value of the recycle delay T_R . The results are shown in Fig. 3.4 for $T_R = 500$ ms. The total integral intensity of the ^1H NMR spectrum for NR1 was measured as a function of θ . For $T_R = 500$ ms, a maximum is detected at $\theta = 60^\circ$.

The measurement of longitudinal magnetization relaxation times (T_1) for each functional group in NR is important for setting the optimum pulse flip angle. Moreover, the amplitude of the stimulated echo is encoded by the longitudinal relaxation times. The inversion recovery method under MAS was used for measurements of $T_1^{(i)}$, where $i = \text{CH}$, CH_2 , and CH_3 . The results are shown in Fig. 3.5. The longitudinal relaxation times are: $T_1^{(\text{CH})} = 0.70$ s, $T_1^{(\text{CH}_2)} = 0.58$ s, and $T_1^{(\text{CH}_3)} = 0.67$ s. The relative difference between longitudinal relaxation times of CH and CH_2 groups is of the order of 17 % only. Moreover, the T_1 values of the CH and CH_3 groups are very close (cf. Fig. 3.5). Therefore, the optimum values for the pulse flip angle θ are not very different for CH, CH_2 and CH_3 groups. Hence, we will take the same value of $\theta = 60^\circ$ for all NR samples, regardless of the investigated functional group.

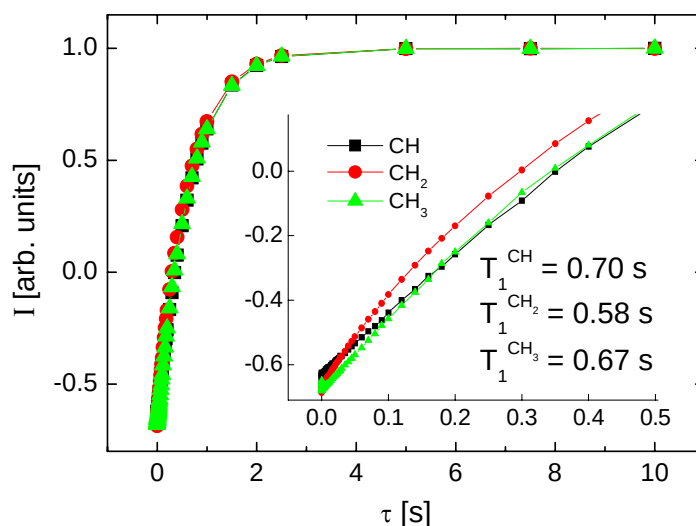


Fig. 3.5 High-resolution ^1H longitudinal relaxation by inversion recovery for NR1 under MAS at $\nu_R = 10$ kHz. The inset shows the differences in the initial increase of longitudinal magnetization of each functional group.

Proton high-resolution rotor-synchronized stimulated echo decays for CH, CH_2 , and CH_3 groups of cross-linked NR1 and NR7 are shown in Fig. 3.6. A crossover of the decay curves is present for all functional groups for the mixing time in the 400 - 500 ms region. This can be explained by the effect of longitudinal magnetization relaxation that is faster for NR7 than for NR1. The T_1 values of 600 - 700 ms were measured for NR1 (see Fig. 3.5), which are close to the values where the crossover of the decay curves occurs.

The most interesting part of the stimulated echo decays is the initial part that carries information about the segmental motions affected by the cross-linking. The decays of each functional group of NR depends on the local residual second van Vleck moment and the correlation time or a distribution of correlation times describing segmental and local motions. For the weakly cross-linked NR1 the decays of all functional groups in the full time regime

investigated can be fairly well approximated by an exponential decay (Fig. 3.6). This is not valid the higher values of cross-link density (Fig. 3.6).

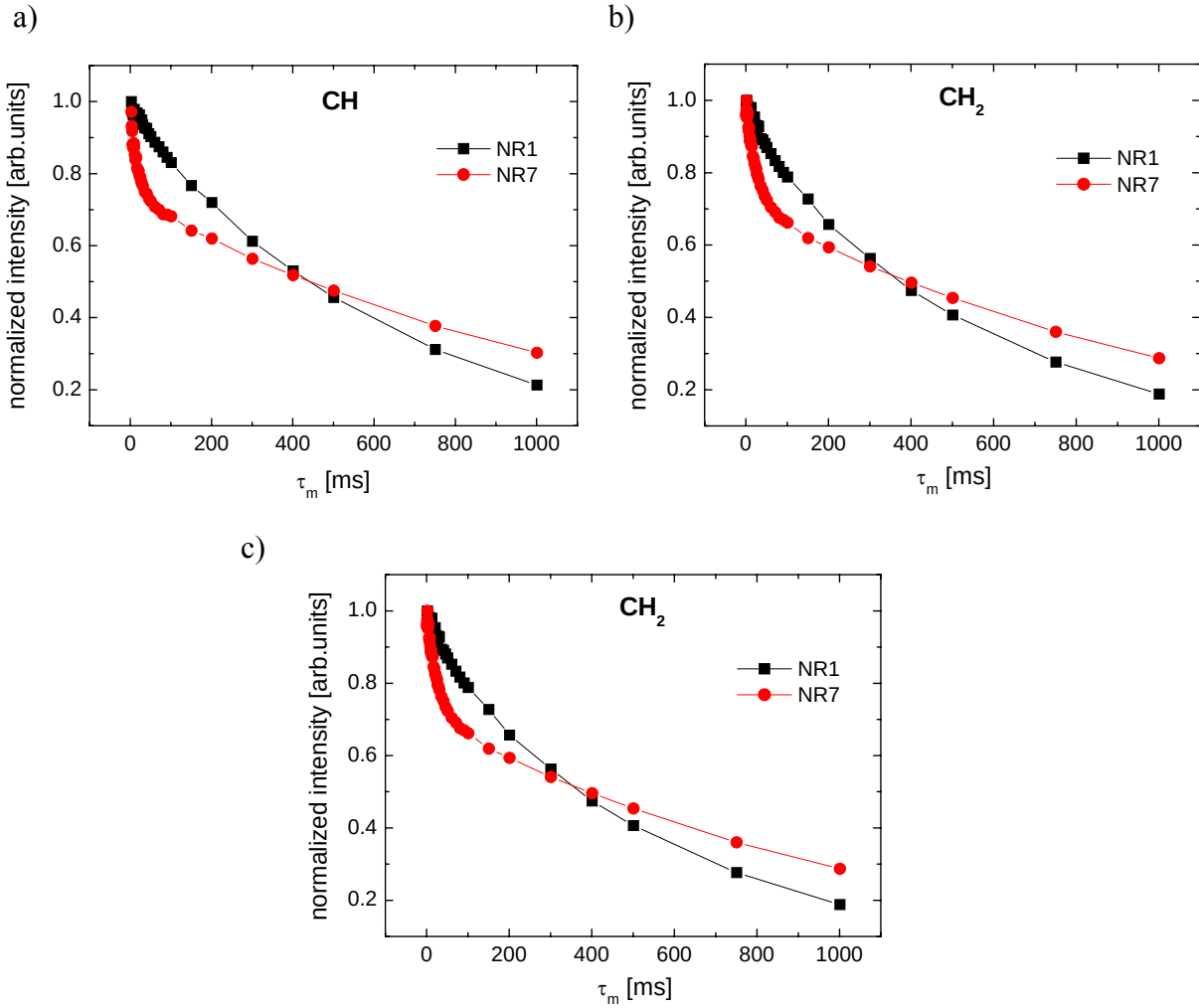


Fig. 3.6 Proton high-resolution rotor-synchronized stimulated echo decays for a) CH, b) CH₂ and c) CH₃ of NR1 and NR7. The lines connecting the data points were drawn for the eyes.

The dependence of the rotor synchronized stimulated echo intensity on the mixing time was fitted by

$$y = A_1 \cdot \exp(-R_1 t^2) + A_2 \cdot \exp(-R_2 t), \quad (3.16)$$

where $A_{1,2}$ are the amplitudes of the two different functional decays and $R_{1,2}$ are the rates of these decays. The first function in the right-hand side of Eq. (3.16) describes the Gaussian contribution to the elastomers network response and the latter function is related to the liquid-like behavior of the network. It can be seen from Fig. 3.7 that the echo decays can be relatively accurately fitted with the Eq. (3.16).

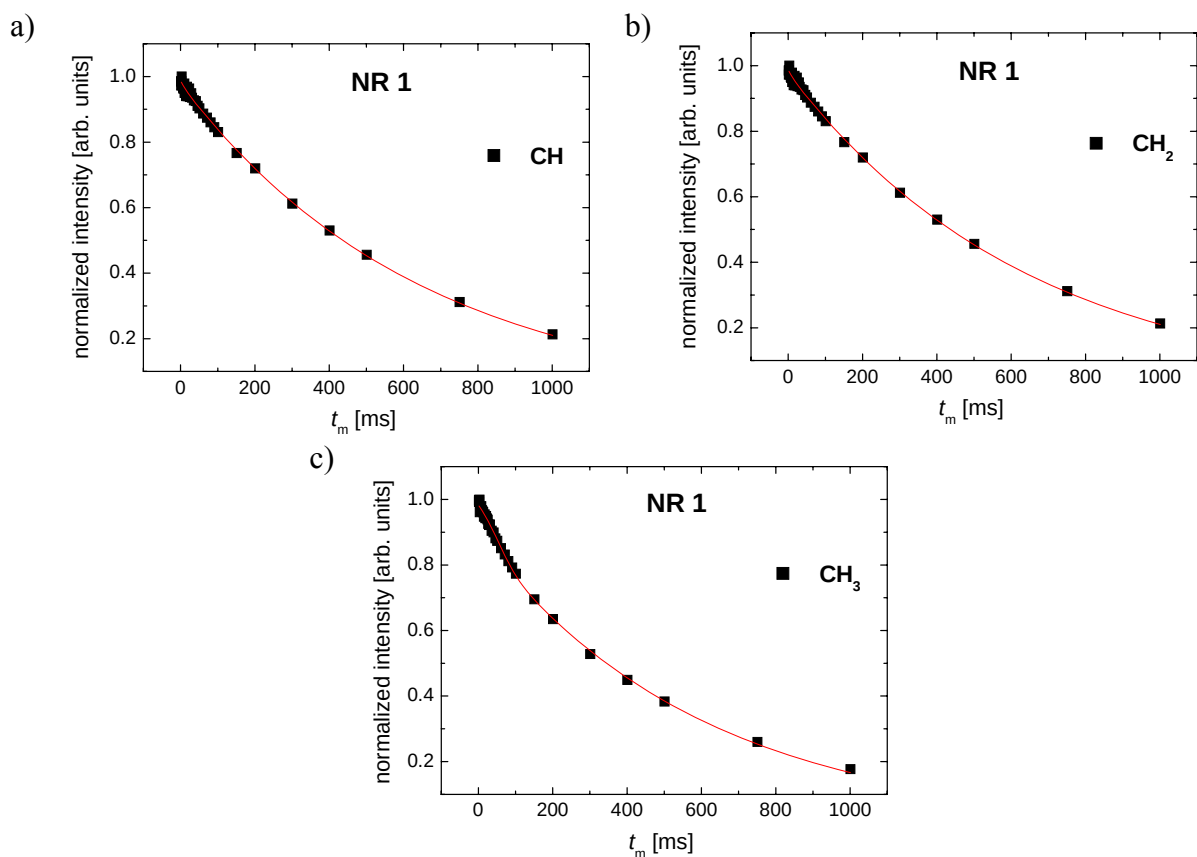


Fig. 3.7 Fits of the rotor-synchronized stimulated-echo decays for a) CH, b) CH₂ and c) CH₃ groups for NR1 using the function from Eq. (13.6).

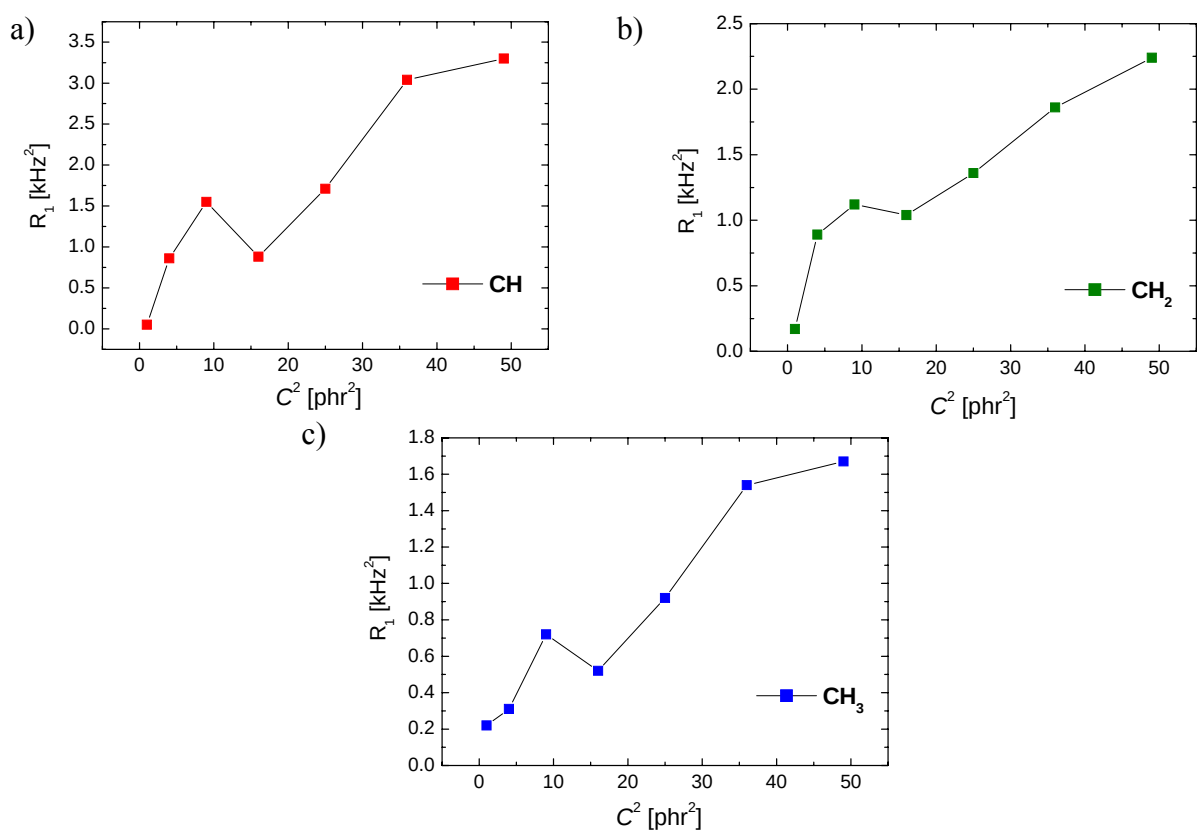


Fig. 3.8 The rate of the Gaussian decay R_1 for each functional group, as a function of C^2 .

The rate of the Gaussian decay R_1 can be correlated with the residual dipolar couplings. It was shown [Dem1] that, for elastomers with a low to medium degree of cross-linking, R_1 is proportional to the square of the residual dipolar couplings strength. As discussed before (see section 3.3.3), this quantity changes proportionally to C^2 [Dem9]. In Fig. 3.8 the values of R_1 for each functional group are shown as a function of C^2 . Two features of these plots are evident: (i) at small values of cross-link density, a strong deviation from the expected linear dependence is present due probably to the continuation of the cross-linking reaction after the vulcanization process; (ii) for larger values of C , the deviation from the linear dependence is due to the non-Gaussian statistics of the end-to-end vector [Dem9]. Moreover, a deviation from the stated cross-link density due to post curing could be also present. It can be noted that ^1H residual dipolar couplings measured by R_1 for CH groups are slightly larger than those of CH_2 and CH_3 . This can be understood by referring to the high-resolution DQ spectrum of synthetic polyisoprene from Fig. 5 in Ref. [Dem4]. It is clear that dipolar interactions of inter-segmental CH groups and strong dipolar interactions with the protons of the CH_2 and CH_3 groups are present, making the overall residual dipolar couplings larger for the CH group.

We can now evaluate the gain in time obtained from the above two-dimensional, time-domain / frequency-domain experiment for the case of elastomers. If the NMR experiments are made at high-magnetic fields under MAS, the signal-to-noise ratio is good, taking into account that a large amount of sample is available. In this case the gain in time is just the ratio between the recycle delays of the standard experiment (T_R^{st}) and the experiment made with the Ernst angle (T_R^{EA}). For the experiment reported here, this ratio is of the order of 10. Therefore, if large series of samples have to be investigated for research or quality control, the gain in time can be substantial, allowing property-structure correlations to be obtained in reasonable time.

3.5 Conclusions

The use of fast multidimensional NMR methods to characterize the elastomers is important due to the necessity to investigate large series of materials or to make real-time experiments. A simplification of such experiments can be obtained if just one frequency dimension is considered together with the mixing time dimension. Such a method, based on the rotor synchronized MAS stimulated echo decay is discussed above. It represents a new method to

obtain information about the residual dipolar couplings of each functional groups of an elastomer monomer. A limitation of this method regards the fact that the intergroup residual dipolar couplings are mixed together with the intragroup couplings. However, an important feature of ROSY-SED is the possibility to speed-up data acquisition. It was shown that the method can give a faster access to information by using the Ernst angle approach, the gain in time being of about one order of magnitude.

With the ROSY-SED method discussed above one is able to investigate slow segmental motions in elastomers that can be correlated afterwards with the viscoelastic properties. The method has been applied to investigate site-selective ^1H residual dipolar couplings in a series of cross-linked natural rubber samples. The results show that the ^1H residual dipolar couplings have indeed different values for each functional group in the NR monomer, including here both intra- and inter-molecular couplings. The theory discussed in section 3.3 shows that these residual dipolar couplings should increase with the square of cross-link density. Our preliminary experiments show that this increase is present, but the derivation of a more accurate functional dependence should be the subject of further investigations.

3.6 References

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4 Morphology and properties of injection molded isotactic polypropylene / silica nanocomposites prepared via *in situ* sol-gel technology

4.1 Introduction

Various experimental methods have been used to determine the crystallinity, phase composition, mobility, and domains thickness of semi-crystalline polymers. The most frequently used methods for estimating the degree of crystallinity are differential scanning calorimetry (DSC) [Man1, Mat1], density measurements [Chi1], X-ray diffraction [Rul1, Rul2, Von1, Wun1] and nuclear magnetic resonance (NMR) [Ber1, Kit1, Ear1, Tan1, Tan2, Dad1, Sch1]. Each of these methods is based on a different physical property, and gives rise to a different definition of the crystalline phase [Isa1]. Although the degree of crystallinity is a quantitative concept, different measurement techniques on exactly the same sample do not always yield the same value. There are several reasons for these apparent differences. They can be attributed in the part to different selectivity of the various techniques to the two major regions, i.e., crystalline and amorphous. In addition, the contribution of the interface to the result of measurement must be taken into account. The NMR studies on semi-crystalline polymers have shown the existence of an intermediate non-crystalline phase associated with the lamella structure [Tan1, Tan2, Dad1, Sch1]. This region is characterized by a degree of order perpendicular to the lamellae surface but disorder in the lateral direction. The interface is important from a theoretical point of view and is a key factor in determining the overall crystalline structure, the morphology and, thus, the mechanical properties.

Polymeric / inorganic nanocomposites, in which at least one of the components has a dimension smaller than 100 nm, have attracted much attention nowadays for their special properties and industrial applications [Bee1, Inn1, Int1, Nov1]. The inclusion of nano-sized particles with huge surface area and often anisotropic geometry in a polymer matrix leads to tremendous changes in morphology and performance. Significant improvements in thermal stability, flame retardancy, and mechanical and dielectric properties have been observed at low filler volume fraction [Bre1, Man2, Stu1, Tre1, Yu1, Sam1].

Nanoscale silica particles are among the most widely used reinforcing fillers. There are three principal procedures commonly employed to disperse nanoparticles in a polymeric matrix: (a) blending in solution [Hsu1, Hon1]; (b) blending in melt [Plu1, Yud1]; (c) *in situ* sol-gel processing [Zha1, Muh1, Jai1].

Nanoscale colloidal silica is commercially available in both aqueous and organic solutions. Direct blending the silica and polymer in a common solvent provides a convenient route to form polymer / silica hybrid materials. This solution process is simple and yields high-quality nanocomposites; however, it is applicable only for certain types of polymers, and cannot be applied for the big-scale manufacturing processes of thermoplastics.

The melt blending method is environmentally benign due to the absence of organic solvents, and it is also compatible with current industrial processes, such as extrusion and injection molding. Due to the lightness of silica nanoparticle powder, blending it with molten polymers appears to be a difficult procedure, and because of the poor compatibility of hydrophilic silica nanoparticles with conventional polymer matrices this method can hardly result in nanocomposites without particle agglomeration. Nevertheless, melt blending for nanocomposite preparation has been developed successfully when the silica particle surface has been substituted with long alkyl chains [Rua1, Gar1].

In situ sol-gel technology is based on mixing of a silica precursor with a polymer and subsequent condensation of the precursor molecules. In a classical *in situ* sol-gel process hydrolysis and then polycondensation of alkoxysilanes takes place under acid or basic conditions in the solution of polymers [Ran1, Sug1, Ala1, Alt1]. This method is, however, not suitable for practical application due to the usage of relatively big amounts of solvents. Sol-gel reactions of tetraethoxysilane (TEOS) in molten polypropylene (PP) [Miz1], and of tetrapropoxysilane (TPOS) in molten ethylene vinyl acetate copolymer (EVA) [Phe1] have been reported. Because of the slow diffusion of TEOS in the highly viscous PP melt, the silica particles are small and homogeneously dispersed in the PP substrate. The reactive processing of EVA with TPOS was a two-step process with the need of dibutyltin oxide as a transesterification catalyst, and yielded quite small particles. However, due to the volatility of TEOS and TPOS, the SiO₂ content in the polymer can hardly be controlled, and it is difficult to produce composites with high inorganic content. An *in situ* sol-gel process for the preparation of PP/silica nanocomposite, where porous PP was immersed in silica sol, has been reported as well [Jai1]. This method is obviously not applicable for a large scale production.

In spite of the many routes for the preparation of polymer/inorganic nanocomposites reported in the literature, these approaches suffer from the multi step procedure and the need

of water and organic solvents in the sol-gel process. Emerging from a collaboration with Dr. Xiaomin Zhu from DWI at RWTH-Aachen, a new approach is proposed here, which is based on a rather well defined precursor polymer for silica, i.e., hyperbranched polyethoxysiloxane (PEOS) [Me11], that can be employed in thermoplastic processing aimed at the development of a solvent-free sol-gel technology for the in situ formation of nanoscale filler particles. Isotactic PP, a commercially available and widely used polymer, is selected as the matrix polymer in this study. The aim of the present work is to investigate the effects of the SiO₂ nanoparticles on the morphology, phase composition, polymer chain motions and the domain thickness of iPP. For the first time, the gradient in the chain dynamics at the interface was measured using ¹H spin-diffusion NMR experiment. The correlation of the NMR results with SAXS and WAXS, as well as with DSC and tensile measurements is also discussed.

4.2 Experimental

4.2.1 Samples

Hyperbranched polyethoxysiloxane (PEOS) was prepared in DWI at RWTH-Aachen using a stoichiometrical one to one reaction mixture (Fig. 4.1) of tetraethoxysilane (TEOS) and acetic anhydride with 0.3 mol % of titanium trimethylsiloxide catalyst (relative to TEOS). The mixture was heated to 135° C in a silicon oil bath under intensive stirring. The resulting ethyl acetate was continuously distilled off. The supply of heat was continued until the distillation of ethyl acetate stopped. Afterward, the product was cooled to room temperature and dried in a vacuum for 5 h. A yellowish oily liquid was obtained. The volatile fractions were removed using a thin-film evaporator operating at 150° C and in vacuum of 10⁻² mbar.

Isotactic polypropylene (MOPLN, HF500N) was obtained from Basell AF, and used as received. Aluminum isopropoxide (98+%, Aldrich), sodium hypochlorite (aqueous solution containing 13% of free chlorine, Acros) and ruthenium (III) chloride hydrate (Fluka) were used without further purification.

PP/SiO₂ composites were prepared at DWI in a 15 ml co-rotating twin-screw microcompounder (DSM Xplore) operating at 200° C under nitrogen atmosphere. This apparatus mimicks the mixing behavior of large twin-screw extruders and, furthermore, allows a continuous processing procedure. The experimental set-up is schematically depicted in Fig.4.2. PP, PEOS and aluminum isopropoxide were fed together into the

For the injection molding, the melting temperature was 200 °C, and the mould was heated to 60 °C. The weight fraction of PEOS content was varied from 0 to 20 wt%. The prepared samples are listed in Table 4.1.

Table 4.1 PP/silica samples prepared via *in situ* conversion of PEOS in PP melts

Sample	PP (g)	PEOS (g)	Aluminum isopropoxide (g)	PEOS content	SiO ₂ content (calc.)	SiO ₂ content (TGA)
1	12.0	0.0	0	0	0	0
2	11.4	0.6	0.012	5 wt%	2.6 wt%	1.7 wt%
3	11.1	0.9	0.018	7.5 wt%	3.9 wt%	3.5 wt%
4	10.8	1.2	0.024	10 wt%	5.3 wt%	3.8 wt%
5	10.2	1.8	0.036	15 wt%	8.1 wt%	6.9 wt%
6	9.6	2.4	0.048	20 wt%	11.1 wt%	9.03 wt%

4.2.2 Characterization methods

Thermogravimetric analysis (TGA) measurement was performed using a Netzsch TG 209c unit operating under nitrogen atmosphere. 20-30mg of samples were placed in standard Netzsch alumina 85 μ L crucibles and heated at 10 K/min to 600 °C. Before each measurement baseline correction was performed with an empty crucible.

Size-exclusion chromatography (SEC) analyses were conducted with a high-pressure liquid chromatography pump (LC 1120, Polymer laboratories) and an evaporative light scattering detector (PL-ELS-1000, Polymer laboratories). The eluting solvent was chloroform (Fisher Scientific). The flow rate was 0.8 mL/min. The sample concentration was around 5 mg/mL. The setup consisted of four MZ-DVB gel columns with the nominal pore sizes of 50, 100, 1000, and 10 000 Å. Calibration with polystyrene standards was used to estimate the molecular weight.

Zero-shear viscosity η_0 values for the liquid samples were obtained from a controlled stress rheometer (Rheometric Scientific DSR). The sample was placed on a 25 mm plate, electrically heated to the desired temperature, and the corresponding cone was lowered into position. The measurement was performed at 25 ± 0.1 °C.

Differential scanning calorimetry (DSC) was conducted on a Netzsch DSC 204 unit equipped with a liquid nitrogen cooling accessory unit (Netzsch CC200 supply system). Indium and palmitic acid were used as calibration standards. Samples (typical weight, 5 mg) were enclosed in standard Netzsch 25 μ L aluminum crucibles. The measurement was carried

out at heating and cooling rate of 10 K/min from -50 °C to 200 °C under a continuous nitrogen purge (50mL/min). Three successive runs (heating-cooling-heating) were performed for each sample.

The mechanical testing of the injection molded standard specimens (ISO 527-2 5A) was done using a tensile testing machine (Rheometric Scientific Minimat 2000) with a 1000 N load cell at a cross-head speed of 1 mm/min at 22 °C and 55 % of relative humidity. Due to the length limitation of this device the measurements of elongation at break were performed on a Zwick 1425 tensile tester with a 2000 N load cell. The measurement condition remained the same. At least 5 measurements were performed for each sample.

Transmission electron microscopy (TEM) analysis was conducted on a Zeiss-Libra 120 microscope operating at 100 kV in the bright-field mode. Samples were prepared by microtoming thin sections on a Reichert ultramicrotome according to the literature [Li1]. The sample bars cut from the tensile testing specimens were trimmed first with a razor blade and then with the ultramicrotome equipped with a glass knife. An extremely smooth trapezoidal top was obtained. The trimmed bars were stained in the vapor of ruthenium tetroxide obtained from ruthenium trichloride hydrate in an aqueous solution of sodium hypochloride. After staining, the bars were washed in a 3% aqueous solution of sodium periodate and then in distilled water, and finally were dried in a desiccator. The final ultrathin sections with thickness less than 150 nm as indicated by the interference color were obtained at ambient temperature with a diamond knife (45°, Diatome). The sections were transferred on copper grids and analyzed.

All NMR experiments were conducted with a Bruker DSX spectrometer operating at a proton resonance frequency of 500.44 MHz. Small grains of samples were inserted into the 4 mm MAS rotor, to avoid chain orientation produced in the samples by molding extruder. The data were collected for static samples at 25° C, which is above the glass transition temperature for iPP. This provides high contrast in the NMR experiments to discriminate the chain mobility of different fractions. The duration of the ^1H 90° pulse was about 5 μs and the dwell time was set to 1 μs . A recycle delay of 5 s was used in all cases. The dead time of the spectrometer is 5.5 μs .

The phase composition, the chain mobility, the second Van Vleck moments, and the thickness of the domains, were investigated with the help of three different solid-state ^1H NMR methods: (i) wide-line NMR spectroscopy, (ii) double-quantum (DQ) build-up curves and (iii) spin-diffusion. Using the DMFIT program [Mas1] the experimental ^1H wide-line NMR spectra were decomposed into three components for pure PP and four components for

PP / silica nanocomposites. The broad component of the spectra was approximated by a Gaussian function. The shape of the line with intermediate width (i.e. the interface) was taken as a combination of a Gaussian and a Lorentzian. The spectral fit has shown, that the narrow component of the spectra, which belongs to the amorphous fraction with high chain mobility, can be well described by the Lorentzian function. This is also valid for the very narrow component (~ 1 kHz) that is related to the fast moving protons of the ethoxy groups in hyper-branched poly(ethoxysiloxane).

Proton NMR spin-diffusion measurements were performed following the scheme consisting of a double-quantum (DQ) dipolar filter, a spin-diffusion period, and an acquisition period (Fig. 2.1) [Dem1, Dem2]. A magnetization gradient was created by the dipolar filter that excites DQ coherences and selects mainly the magnetization of the rigid phase. The DQ build-up curves were measured by systematically incrementing the excitation/reconversion time, using a very short DQ evolution period of 5 μ s and a spin-diffusion time of 10 μ s. The value of the excitation/reconversion time used afterwards in the spin-diffusion experiment is $\tau = 7$ μ s.

Solid-state ^{29}Si NMR spectra were obtained with the same Bruker DSX-500 NMR spectrometer, operating at 99.362 MHz ^{29}Si resonance frequency, in static conditions (for PEOS liquid samples) or under magic-angle sample spinning (for solid PEOS samples). The spectra were recorded during a ^1H decoupling pulse of 50 ms, following the excitation with a 6 μ s long radio-frequency pulse. For the measurements, 0.015 mol/L chromium(III) acetylacetonate (purum, Fluka) was dissolved in the liquid PEOS samples as a paramagnetic relaxing agent, to shorten the recycle delays to 10 s. The ^{29}Si NMR spectra were recoded at room temperature with 6000 scans and a dwell time of 20 μ s. The spectra were corrected for the background signal from the probe by numerical subtraction.

4.3 Results and discussion

4.3.1 Characterization of “one-pot” synthesized PEOS

Silicon is a very important building element for the dendritic polymers due to the versatility of organosilicon chemistry [Fre1, Lan1]. Among various silicon-containing polymers, polyethoxysiloxanes (often named “ethylsilicates” or “condensed ethylsilicates”) are of

increasing technological interest as processable precursors for silica [Abe1]. Typically they are condensation products of tetraethoxysilane (TEOS) with water, but the products obtained contain silanol groups, which can undergo further condensation and thus cause aging and changes in the properties upon storage [Bou1]. Recently, a controlled synthesis of hyperbranched polyethoxysiloxanes (PEOS) from triethoxysilanol and acetoxytriethoxysilane AB_3 monomers [Jau1] has been published. The polymers obtained containing no hydroxyl groups. Hence, they are stable upon long-term storage. However, the need of an intermediate step to obtain and isolate the AB_3 monomers and the complicated purification process required to obtain the final product make this route unsuitable for a large scale production.

A new one-pot synthesis of PEOS based on the catalyzed condensation reaction of TEOS with acetic anhydride (Fig. 4.1) is introduced here, which is capable of obtaining fully soluble or liquid products of high molecular weight in a really controllable way.

Using 1H NMR, it has been demonstrated that the condensation reaction from Fig. 4.1 is complete (Fig. 4.3), without the presence in the final product of any acetoxy groups coming from the acetoxytriethoxysilane AB_3 monomers, as for the previously discussed “two-steps” synthesis.

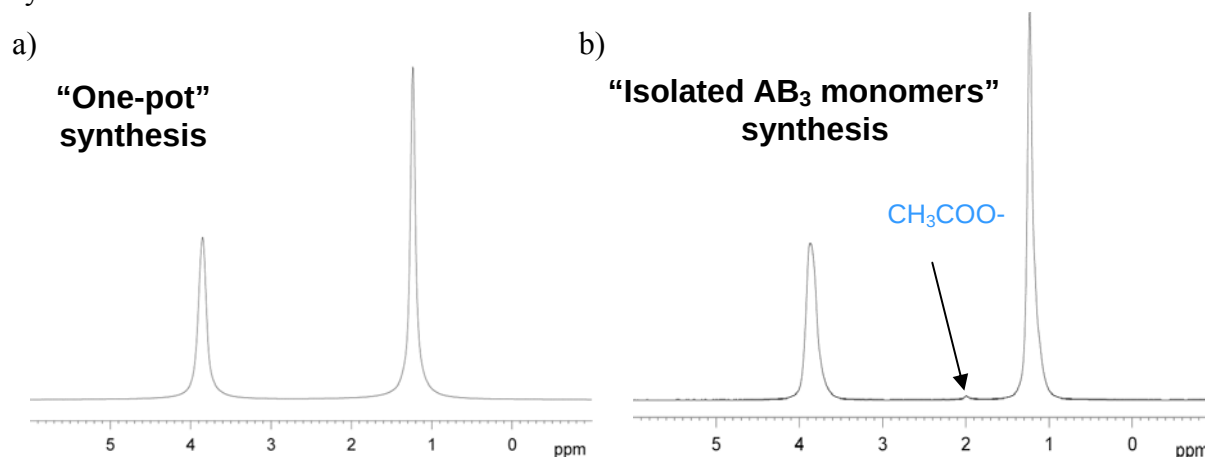


Fig. 4.3 Proton NMR spectra of PEOS products obtained using a) one-pot synthesis reaction and b) “isolated AB_3 monomers” synthesis reaction.

The ^{29}Si NMR spectroscopy has been used to prove the hyperbranched structure of PEOS. The ^{29}Si NMR spectrum of PEOS obtained from a stoichiometrical one to one mixture of TEOS and acetic anhydride with 0.3 mol % of catalyst shows five groups of peaks (Fig. 4.4). These peaks can be assigned (from left to right) to silicon atoms bearing: four ethoxy groups Q_0 (-81.74 ppm, TEOS), three ethoxy groups Q_1 (-88.70 ppm, terminal units), two ethoxy groups Q_2 (-96.1 ppm, linear units), one ethoxy group Q_3 (-102.7 ppm, semidendritic units), and no ethoxy group Q_4 (-110.0 ppm, dendritic units) [Jau1].

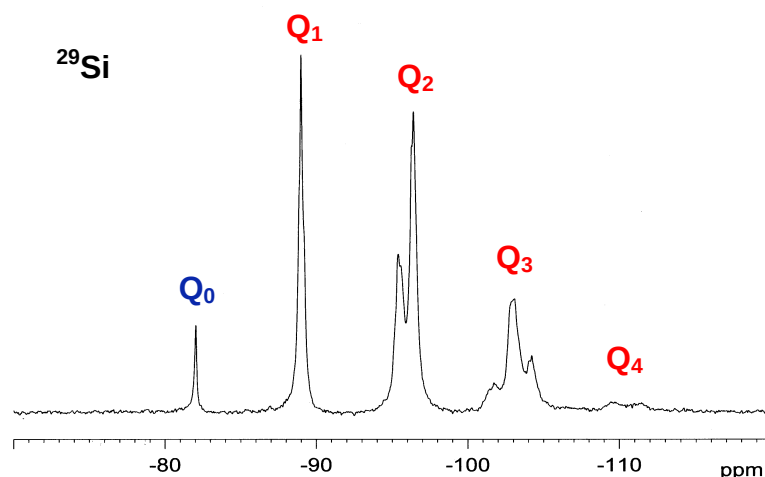


Fig. 4.4 Solid-state ^{29}Si NMR spectra of PEOS obtained from a stoichiometrical one to one mixture of TEOS and acetic anhydride with 0.3 mol % of catalyst.

The areas of the individual peaks allow the determination of the relative amounts of all different silicon atoms in the polymer. The degree of branching (DB) was calculated according to Eq. (4.1), where it is expressed as a ratio of the actual growth direction R in a macromolecule to the maximum possible growth directions $R_{\max}$ [Höl1]. The calculated DB value for the above-mentioned PEOS was 0.48 (see Table 4.2). This value as well as the distribution of different building units is close to the theoretical value expected for equal reactivity of all ethoxy groups [Höl1].

$$DB = \frac{R}{R_{\max}} = \frac{2Q_4 + Q_3}{\frac{2}{3}(3Q_4 + 2Q_3 + Q_2)} = 0.48 \quad (4.1)$$

It can be expected that an excess of acetic anhydride will improve the degree of condensation and yield a crosslinked product eventually. A maximum degree of condensation without gelation, i.e., maximum branching and even intramolecular loop formation, will be most favorable for most applications while the product still remains liquid. We found that under the same reaction conditions liquid and soluble PEOS products were obtained at molar ratio (f) of acetic anhydride to TEOS up to 1.2 (Scheme 4.1). At $f = 1.3$, a solid gel was formed.



Scheme 4.1 Reaction of TEOS with Acetic Anhydride at Different Molar Ratio (f)

Silicon-29 NMR spectroscopy was used to follow the structure change in PEOS products with different f . Figure 4.5 shows the representative ^{29}Si NMR spectra of PEOS obtained at $f = 1$, $f = 1.10$ and $f = 1.20$.

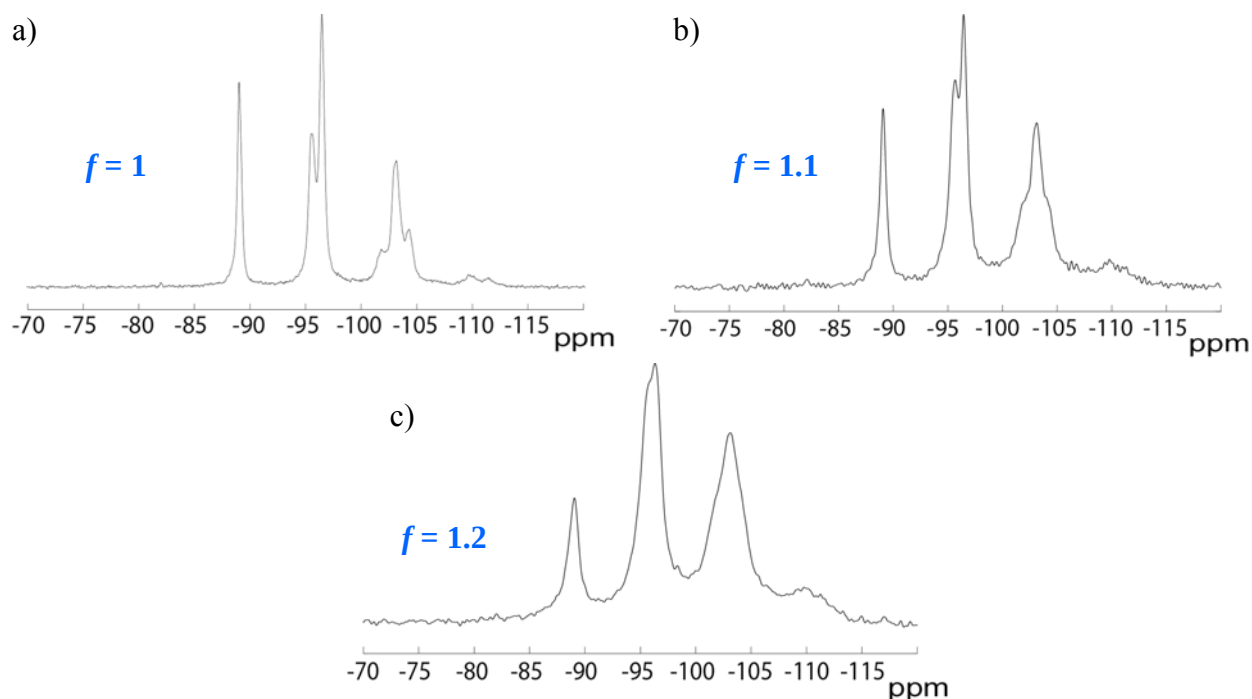


Fig. 4.5 Silicon-29 NMR spectra of PEOS obtained at molar ratio of acetic anhydride to TEOS a) $f = 1$, b) $f = 1.10$, and c) $f = 1.20$.

Table 4.2 summarizes the ^{29}Si NMR data of PEOS obtained at different f . These data show that the distribution of different building units changed with increasing f . The relative amount of linear units Q_2 remained almost constant, and the amount of the semidendritic and dendritic groups increased at the expense of terminal groups; the degree of branching, hence, also increased.

The dependence of the degree of branching on the molar ratio of acetic anhydride to TEOS is shown in Fig. 4.6.

Table 4.2 Relative contents of different building units of PEOS obtained at different molar ratio of acetic anhydride to TEOS (f)

f	terminal, Q_1 [%]	linear, Q_2 [%]	semidendritic, Q_3 [%]	dendritic, Q_4 [%]	DB
1	23.6	42.1	26.9	3.9	0.48
1.05	21.9	43.1	28.4	3.8	0.49
1.10	18.9	42.6	31.7	4.8	0.51
1.15	14.2	42.4	37.3	6.1	0.55
1.20	14.4	39.5	38.5	7.6	0.58
1.30	10.1	42.5	41.0	6.4	0.56

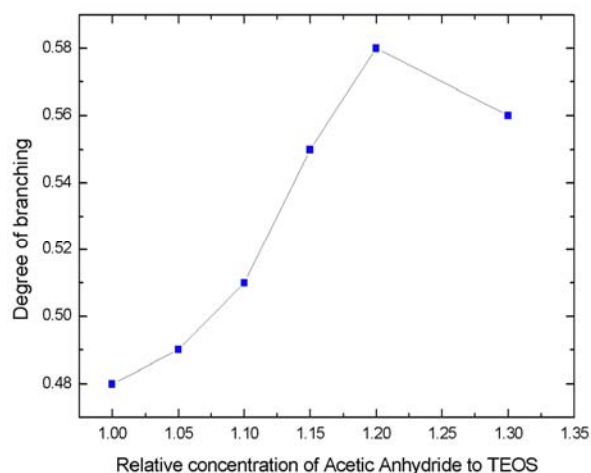


Fig. 4.6 The increase of DB as a function of relative concentration of acetic anhydride to TEOS

Figure 4.7a shows the size exclusion chromatography (SEC) analysis results of PEOS products synthesized at various f . The apparent average molecular weight (compared to polystyrene standard samples), as well as the molecular weight distribution, increases exponentially by increasing f . The condensation reaction became less controlled at higher values of f due to the extended coupling reaction between macromolecules, leading to multimodal distribution of molecular weight. Zero-shear viscosity of PEOS increased exponentially with f as well (Fig. 4.7b). Thus, it is demonstrated that the molecular weight of PEOS in the one-pot synthesis can be tuned by simply varying the reagent ratio f .

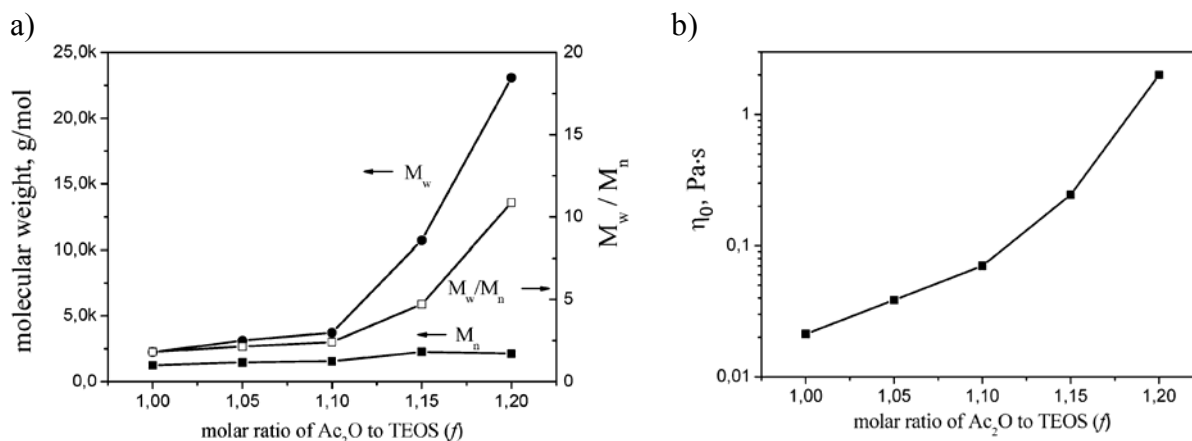


Fig. 4.7 The dependence of the a) number- and weight-average molecular weights obtained by SEC and b) zero-shear viscosity η_0 of PEOS on the molar ratio (f) of acetic anhydride to TEOS.

The SiO₂ content of the final PEOS products has been calculated using ²⁹Si NMR data, and the results were compared with the theoretical values and the values obtained by gravimetry after full hydrolysis (Table 4.3). TGA cannot yield correct SiO₂ content of PEOS due to the SiO₂ loss in the form of TEOS and other volatile oligosiloxanes, which are

evaporated during TGA. To get the right result from gravimetry, the samples were first fully hydrolyzed using a mixture of ethanol and aqueous solution of ammonia (volume ratio 1:1). The solvent was then slowly removed at 80° C, and after calcination in a Muffel oven at 900 °C until a constant mass the residue was weight. It can be seen that the SiO₂ contents determined by gravimetry and ²⁹Si NMR were identical, and for all liquid PEOS products they were also very close to the theoretical values calculated according to Scheme 4.1. The solid gel obtained at $f = 1.30$ has a slightly lower SiO₂ content than the theoretically expected one. This is explained by the incompleteness of the condensation reaction because of the fast solidification process.

Table 4.3 SiO₂ content of PEOS products obtained at different molar ratio (f) of acetic anhydride to TEOS determined by different methods

f	gravimetric SiO ₂ content after full hydrolysis, %	SiO ₂ content according to ²⁹ Si NMR, %	theoretical SiO ₂ content %
1	45.4	45.3	44.8
1.05	45.9	45.8	46
1.10	47.6	47.2	47.4
1.15	48.9	49.6	48.8
1.20	49.5	50.2	50.3
1.30	52.1	50.9	53.7

4.3.2 Polypropylene / silica nanocomposites

In-situ sol-gel conversion of liquid PAOS to solid silica. PEOS (Fig. 4.1) is a unique liquid precursor polymer of silicon dioxide. It is stable upon storage because of the high hydrophobicity and lack of reactive groups like silanol and acetoxysilane. It is miscible with most organic solvents. It should be noted that, after thin-film evaporator treatment, the product does not contain any volatile fractions [Mel1], hence, it can easily be blended with polymer melts at high temperature for the further processing.

It was observed that the solubility of PEOS in PP melt was quite low, less than 0.5 wt%. However, up to 30 wt% PEOS can be mixed into the PP melt to obtain a uniform turbid PP/PEOS blend. PP, PEOS and the catalyst were fed together into the microcompounder (Fig. 4.2). A small amount of aluminum isopropoxide (2 wt% relative to the weight of PEOS) was used as the catalyst for the PEOS conversion. ¹H solid state NMR spectroscopy was used to

monitor the conversion of PEOS in the PP melts. Figure 4.8 demonstrates the change of ^1H wide line NMR spectra during the *in situ* conversion. PEOS displayed quite good signals in solid ^1H NMR spectra even after embedding in PP due to its liquid nature and incompatibility with the matrix. A significant change of the spectra was observed after the conversion. Proton wide-line NMR spectrum of pure PP can be decomposed into three components (Figure 4.8a). These components correspond to the rigid (crystalline), mobile (amorphous) and interfacial phases. The interface domain detected by NMR contains polymer chains with more mobility than rigid domains but less mobility than the amorphous (highly mobile) phase. The separation of these fractions is made based on the chain and segmental motions. Therefore, it is not unexpected that the content in interfacial region is bigger than the content of amorphous phase. The chain mobility can be inferred from the line-width at the half intensity of each spectral component, and the values are 55.5 kHz for rigid fraction, 18.1 kHz for interface and 4.1 kHz for mobile fraction.

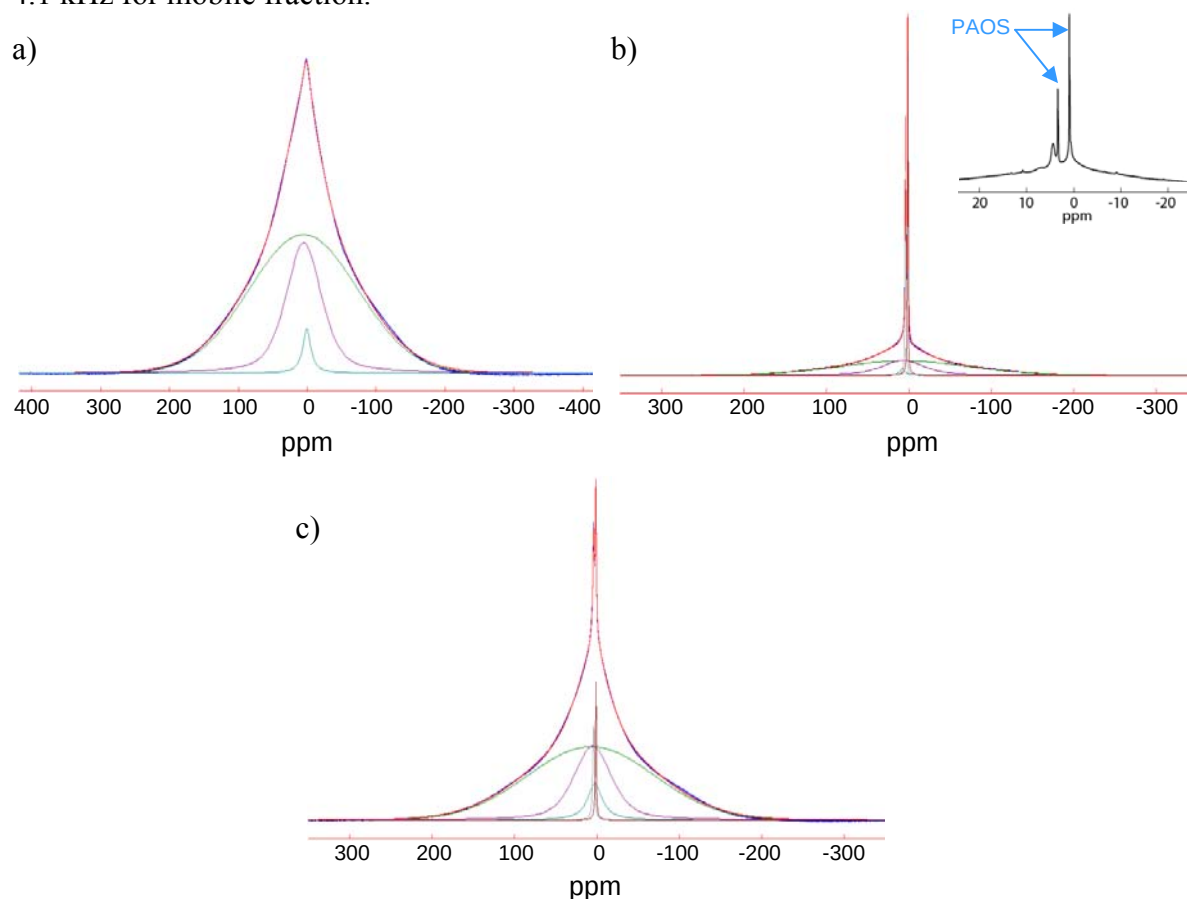


Fig. 4.8 Proton solid state NMR spectra of a) pure PP and b) PP/PEOS composite (20 wt.% PEOS in PP) before and c) after *in situ* conversion.

The ^1H NMR spectra of the PP/PEOS blends as well as the resulting PP/silica composites were decomposed into five components. Besides the components belonging to

pure PP, two narrow peaks were detected at 3.9 ppm and 1.3 ppm that corresponded to CH_2 and CH_3 of ethoxysilane group (see the inset in Fig. 4.8b). Comparing the areas of CH_2 and CH_3 signals before and after conversion, the percentage of the remaining ethoxysilane groups was calculated and is shown in Table 4.4. One can see that despite the high hydrophobicity of PP matrix, the *in situ* conversion of PEOS proceeded to a large extent. The content of ethoxy groups decreases with the increase of PEOS loading. This can be attributed to the increase of the particle size. In these composite materials the hydrophobic ethoxy groups should be located on the surface of the resulting silica particles instead of hydrophilic hydroxyl groups, forming an interface with hydrophobic PP matrix. According to TEM data (Fig. 4.9), the silica particle size increases with the increase of PEOS loading, the specific surface area of the particles, hence, decreases; this can explain why the content of ethoxy group decreases with the increase of PEOS loading.

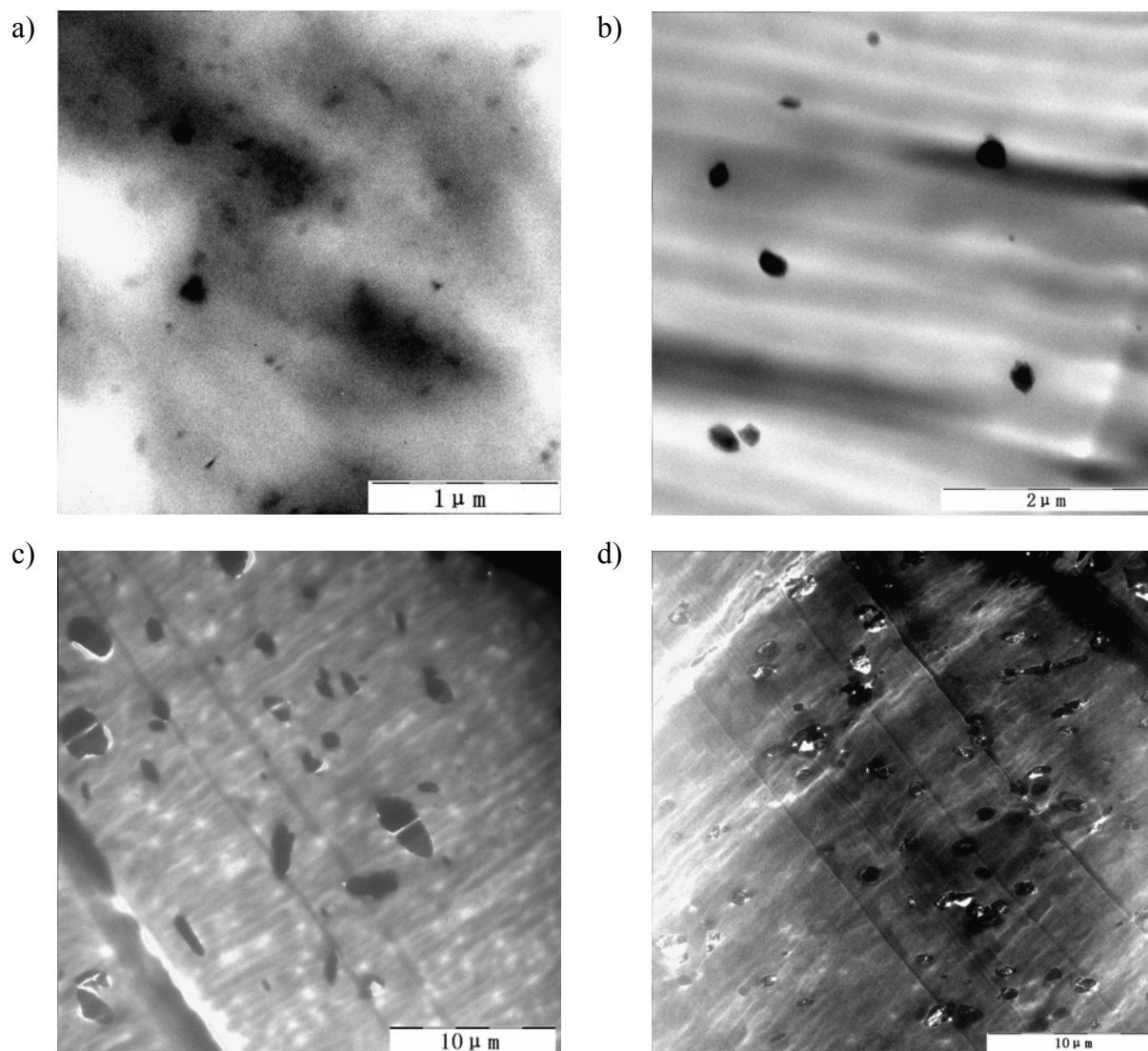


Fig. 4.9 TEM image of PP/silica composites prepared by *in situ* sol-gel technology using a) 5 wt.% PEOS, b) 10 wt.% PEOS, c) 15 wt.% PEOS, d) 20 wt.% PEOS.

Table 4.4 Remaining ethoxy groups after *in situ* conversion of PEOS in PP melts measured by ^1H NMR

PEOS content	5 wt.%	10 wt.%	15 wt.%	20 wt.%
Remaining ethoxy group	34 %	21 %	19 %	16 %

The structure of the PP/silica composites produced via *in situ* sol-gel technology from PEOS was investigated by means of transmission electron microscopy (TEM). The TEM images of PP containing different amount of silica are shown in Fig. 4.9. The sample prepared with small amount of PEOS (5 wt.%) contains silica nanoparticles, which are mainly smaller than 100 nm and are homogeneously dispersed in the polymer matrix (Fig. 4.9a). However, due to the bad compatibility of PEOS with PP, the particle size increased, when more PEOS was fed. With the PEOS content of 10 wt.%, particles of 300 – 400 nm were observed (Fig. 4.9b). At relatively high loading of PEOS (15 and 20 wt.%), silica particles of several micrometers were formed (Fig. 4.9c,d).

Phase composition and chain dynamics in the iPP/SiO₂ nanocomposite by ^1H NMR. Proton wide-line NMR spectra can provide useful information about the effect of SiO₂ on the iPP matrix. The NMR spectra measured for static samples can be decomposed into different components as shown in Fig. 4.8. From such decomposed spectra, the concentration of rigid (r), semi-rigid (i, interfacial) and amorphous (m, mobile) fractions can be obtained as a function of the PEOS concentration. This is shown in Fig. 4.10, together with the total concentration of remaining ethoxy functional groups.

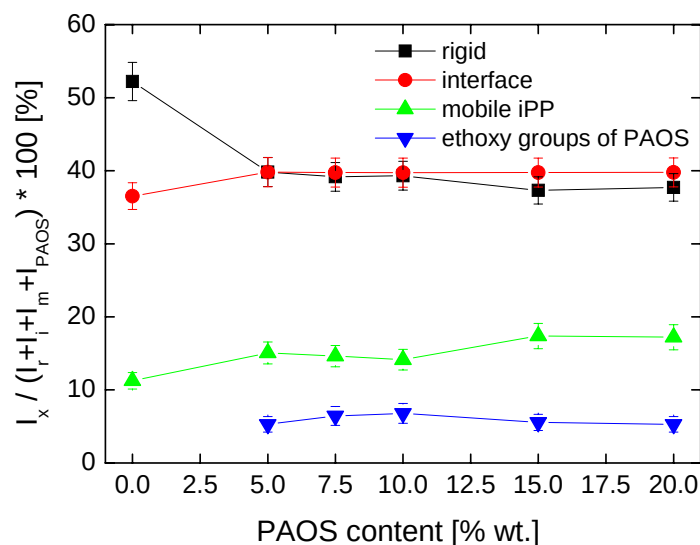


Fig. 4.10 The amount of rigid, semi-rigid, and soft fractions of iPP/SiO₂ composites as a function of PEOS load, measured from ^1H wide-line NMR spectra. The content of non-converted PEOS is also shown.

From the data shown in Fig. 4.10 it is apparent that the amount of all fractions changes slightly with the PEOS content in the investigated range from 5 to 20 wt.%. However, a more noticeable change in the phase composition takes place when comparing iPP and the iPP/SiO₂ composites. The silica network is localized in the amorphous and interfacial regions, so that these fractions grow compared to those in pure iPP. This occurs as a result of a break-down of the rigid fraction, which includes the crystalline phase. It can be also seen that the amount of rigid and interfacial fractions becomes almost the same in the PEOS range of 5 - 20 wt.%. The data presented in Fig. 4.10 show that the deconvolution of the ¹H wide-line NMR spectra is not very sensitive to the increase of the amount of PEOS in the range up to 20 wt.%. The amount of non-converted PEOS is about 3-5 % (Fig. 4.10).

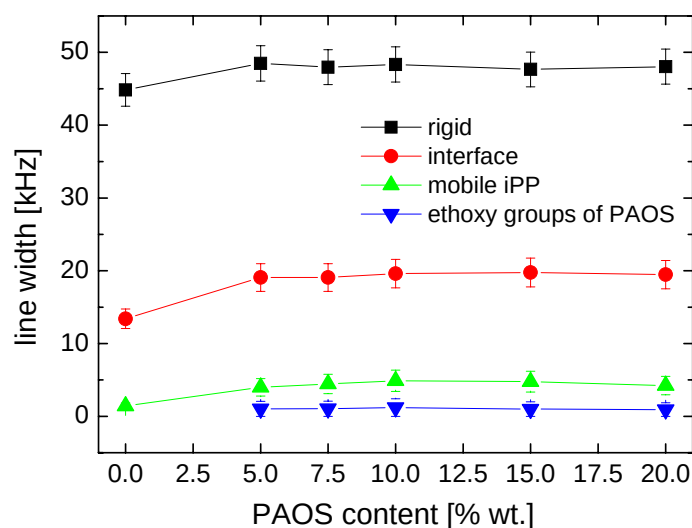


Fig. 4.11 Chain dynamics of the rigid, semi-rigid, and soft fractions of iPP measured from the full line-width at half-intensity of the ¹H NMR spectral components, as a function of PEOS content. The molecular dynamics of the functional groups of non-converted PEOS is also shown.

The presence of the branched polyethoxysiloxane embedded into the iPP matrix restricts the chain motions of all fractions. This is shown in Fig. 4.11, where a more pronounced effect on the spectral components line-width is evident for the interfacial region. As expected, the chain polymer motions are hindered by the presence of silica particles, as compared with the native sample. The chain hindrance and the motions of protons in ethoxy groups are not essentially influenced by the amount of PEOS in the range investigated.

Double-quantum dipolar filter. The spin-diffusion experiments observe the equilibration of spatially heterogeneous magnetization over the sample. A gradient in the magnetization can be created, for example, with a dipolar filter which excites double-quantum (DQ) coherences

[Dem2]. The DQ filter can be set in such a way to select only the magnetization from the most rigid part of a heterogeneous sample. By choosing appropriate excitation/reconversion periods τ (see Fig. 2.1) of the double-quantum coherences, the magnetization corresponding to the stronger dipolar couplings will pass through the filter and that of the weaker dipolar couplings is filtered out. The optimum value of τ can be chosen by recording DQ build-up curves as shown in Fig. 4.12 for iPP and iPP with different contents of PEOS. The maxima of the DQ build-up curves appear at very short excitation/reconversion times τ of about 10-12 μs for all investigated samples. In this range of τ values, the mobile component is completely filtered out as shown below. The slope of the DQ build-up curves in the initial regime of the excitation/reconversion times is related to the residual van Vleck second moment ($\overline{M}_2$) of the rigid fraction.³⁴

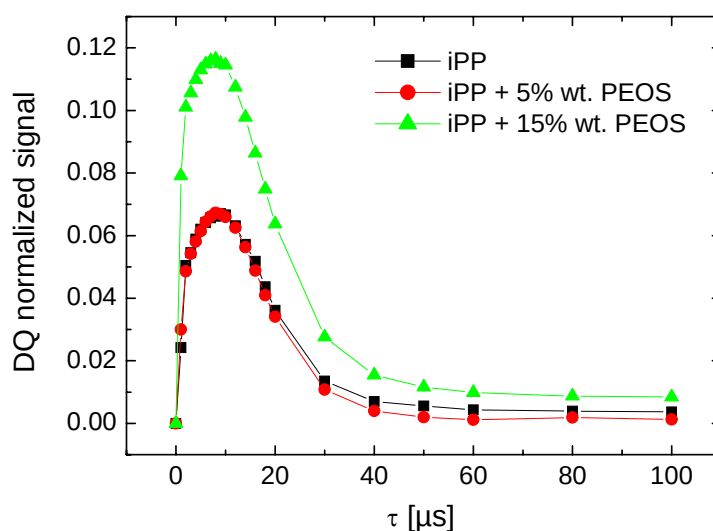


Fig. 4.12 Proton DQ build-up curves for iPP with different content in PEOS. For all samples the maximum occurs in the same region of excitation/reconversion time of about 10 μs .

The DQ filtered NMR spectra recorded for different values of the excitation/reconversion times τ are shown in Fig. 4.13 for iPP with 7.5 wt.% PEOS. For short τ values the DQ filtered ^1H spectrum edits mainly the spin-pairs with the strongest dipolar couplings (Fig. 4.13a). In the region of the maximum of the DQ build-up curves, the pulse sequence edits a dipolar network of many spins corresponding to the crystalline and partially the interface fraction (Fig. 4.13b). The ^1H spectrum in Fig. 4.13c filtered only the NMR signal from the amorphous fraction. The value of $\tau = 7 \mu\text{s}$ has been chosen for the dipolar filter of the rigid domain, which still keeps the filter efficiency close to unity with a reasonable value of the signal-to-noise ratio.

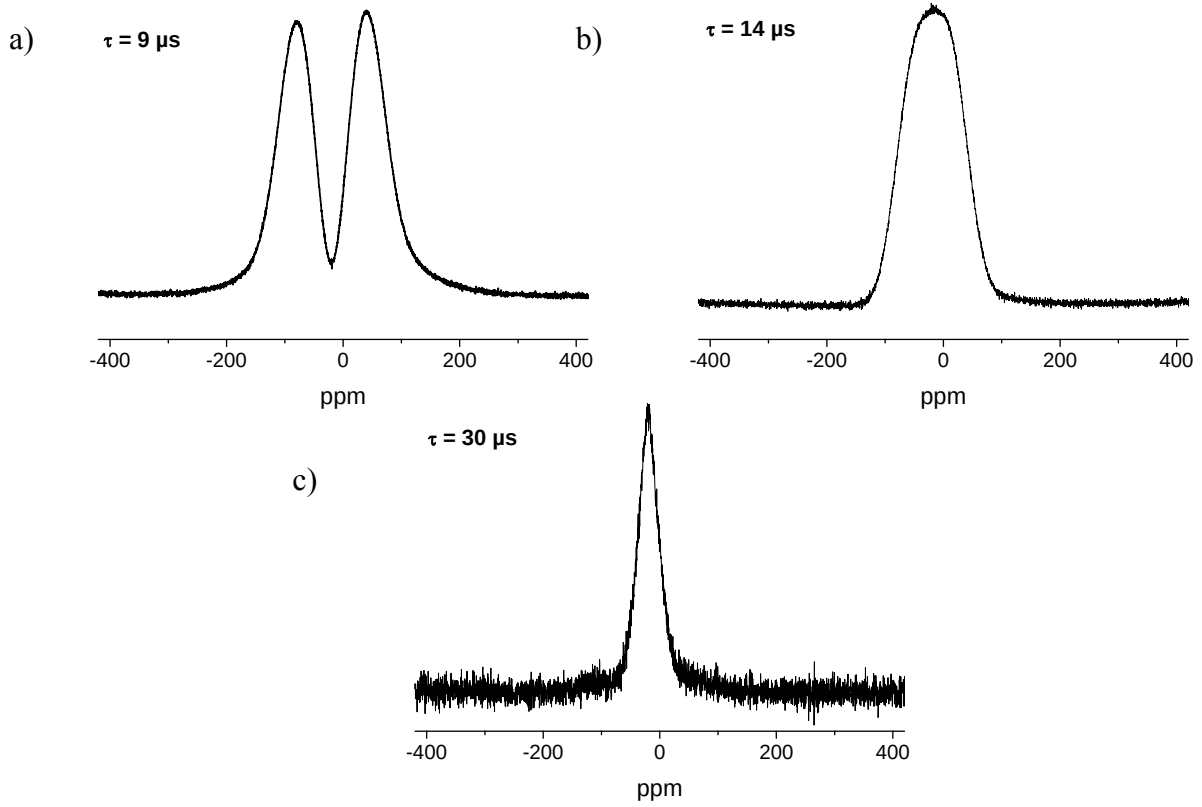


Fig. 4.13 Proton DQ edited spectra for iPP with 7.5 % wt. PAOS for a) $\tau = 9 \mu\text{s}$, b) $\tau = 14 \mu\text{s}$, and c) $\tau = 30 \mu\text{s}$.

Proton residual second van Vleck moments. The measured values of the residual second van Vleck moment ($\langle M_2 \rangle$) using DQ build-up curves (Fig. 4.12) are summarized in Table 4.5. These moments have been obtained by the fit of the normalized DQ build-up curve in the initial time regime by the heuristic function of the form [Dem3]

$$S_{DQ}^{norm}(\tau) \propto \left\{ 1 - \exp\left[-\frac{\overline{M}_2}{2} \tau^2\right] \right\} \exp\left[-\frac{2\tau}{T_2^*}\right], \quad (4.2)$$

where T_2^* is the effective transverse relaxation time.

The residual van Vleck moments measured in this experiment reflect only the ^1H dipolar couplings of the rigid fraction. The $\overline{M}_2$ values increase with the PEOS load, relative to the iPP sample, due to an increase in the chain packing in the rigid fraction. This is consistent with the changes in the rigid component linewidth shown in Fig. 4.11.

Table 4.5 Proton van Vleck second moments of iPP/SiO₂ composites

% wt. PEOS	$\langle M_2 \rangle (2\pi)^2 \text{ [kHz}^2\text{]}$
0	1.1×10^4
5	1.62×10^4
15	2.87×10^4

Proton spin-diffusivities. An accurate analysis of the thickness of domains by NMR spin-diffusion experiments requires three steps. These are: (i) an optimization of a dipolar filter to obtain the highest selectivity to the different phases (see above), (ii) knowledge of the spin-diffusion coefficients (D) for modelling the experimental data, and (iii) proper choice of a model that describes the morphology of the material studied. The spin diffusivities (D) can be expressed in terms of the ^1H local dipolar field, so that the D values are related to the second van Vleck moments [Dem1].

The values of the spin-diffusivities D_R and D_M for the rigid and soft fractions, respectively, can be determined by approximating the NMR line shapes of the rigid and the soft fractions by Gaussian and Lorentzian functions, respectively. The spin-diffusion coefficients can be related to the second van Vleck moment of the NMR absorption lines, which, in turn, are related to the full line-width $\Delta\nu_{1/2}$ at half height (Fig. 4.11).

The equations describing the spin-diffusion coefficients for rigid and mobile regions are given by [Dem1],

$$D_R = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta\nu_{1/2}, \quad (4.3)$$

and

$$D_M = \frac{1}{6} \langle r^2 \rangle [\alpha \Delta\nu_{1/2}]^{1/2}, \quad (4.4)$$

where α is the cut-off parameter of the Lorentzian line, $\Delta\nu_{1/2}$ is the full line width at half height, and $\langle r^2 \rangle$ is the mean square distance between the nearest spins. An estimation of $\langle r^2 \rangle \approx 0.08 \text{ nm}^2$ was made using the Gaussian 03W software package (Gaussian Inc., Pittsburgh PA, 2003).

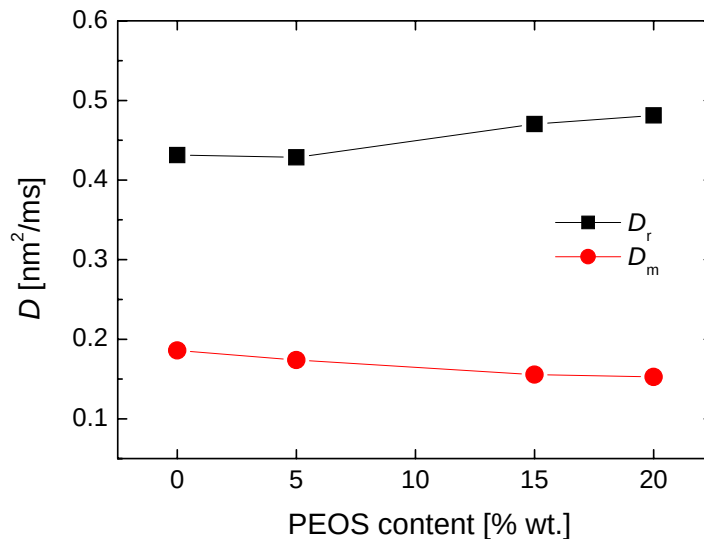


Fig. 4.14 Spin-diffusivities for the rigid and amorphous fractions of iPP with different content in PEOS.

The calculated spin-diffusion coefficients for the rigid and mobile domains using the above equations are shown in Fig. 4.14. As expected, they do not show a dramatic dependence on the content in PEOS.

The transport of z-magnetization oriented along the static magnetic field in a NMR experiment can be described by the diffusion equation in the continuum approximation. The concentration $m(\vec{r}, t_d)$ of nuclear z-magnetization at position $\vec{r}$ in the sample at the moment of time t_d is defined by

$$m(\vec{r}, t_d) = \frac{M_z(\vec{r}, t_d)}{\rho(\vec{r})\Delta V(\vec{r})}, \quad (4.5)$$

where $M_z(\vec{r}, t_d)$ is the total z-magnetization and $\Delta V(\vec{r})$ is the infinitesimal volume around the point defined by the vector $\vec{r}$. The number density of spins is denoted by $\rho(\vec{r})$.

In the limit of isotropic spin-diffusion and spatially constant spin diffusivity the spin diffusion equation has the form

$$\frac{\partial m(\vec{r}, t_d)}{\partial t} = D\nabla^2 m(\vec{r}, t_d). \quad (4.6)$$

The instantaneous NMR observables in a spin-diffusion experiment are represented by the normalized integral intensity $I_i(t_d)/I_0$ of the i^{th} component of the NMR spectrum with the total integral intensity I_0 . More specific the NMR spin-diffusion observables are defined by

$$\frac{I_i(t_d)}{I_0} = \frac{\iiint_{V_i} \rho_i m_i(\vec{r}, t_d) d\vec{r}}{I_0}, \quad (4.7)$$

where V_i is the volume of the i^{th} domain.

The real morphology of iPP/SiO₂ hybrids is cross-hatched, as proved by WAXS. This can be approximated by a square-transverse morphology for the spin diffusion process. Moreover, we assume that the spin-diffusion takes place in a heterogeneous matrix from a source R with low segmental mobility into a finite sink M with larger segmental mobility. The interfacial region is taken together with the amorphous fraction in the following considerations. The relationships describing the time evolution of the integral intensities of the NMR signals $I_R(t_d)$ and $I_M(t_d)$ for a spin-diffusion process of dimensionality $n = 2$ can be obtained from Ref. [Dem4]. The spin magnetization in the source region (R) for a two-dimensional spin-diffusion process is given by

$$I_R(t_d) \approx \rho_R \left[2 \int_0^{d_R/2} m_R(x, t_d) dx \right]^2, \quad (4.8)$$

where ρ_R is the number density of spins of the source R of size d_R and $m_R(x, t)$ is the space and time dependent concentration of the z spin magnetization. For a dipolar filter that selects only the magnetization of the R region, the spin magnetization in the sink region can be written as

$$I_M(t_d) = I_R(0) - I_R(t_d). \quad (4.9)$$

The effect of silica particles on the domain thickness of iPP/SiO₂ composites. Proton wide-line NMR spectra of iPP recorded at three different diffusion times t_d are shown in Fig. 4.15. At short diffusion times mainly the rigid fraction of iPP is observed, as can be seen in Fig. 4.15a for $t_d = 50 \mu s$. Upon increasing the spin-diffusion time, the relative intensity of the rigid fraction in the spectra decreases, and the intensity of the narrow line that originates from the soft amorphous fraction of iPP increases.

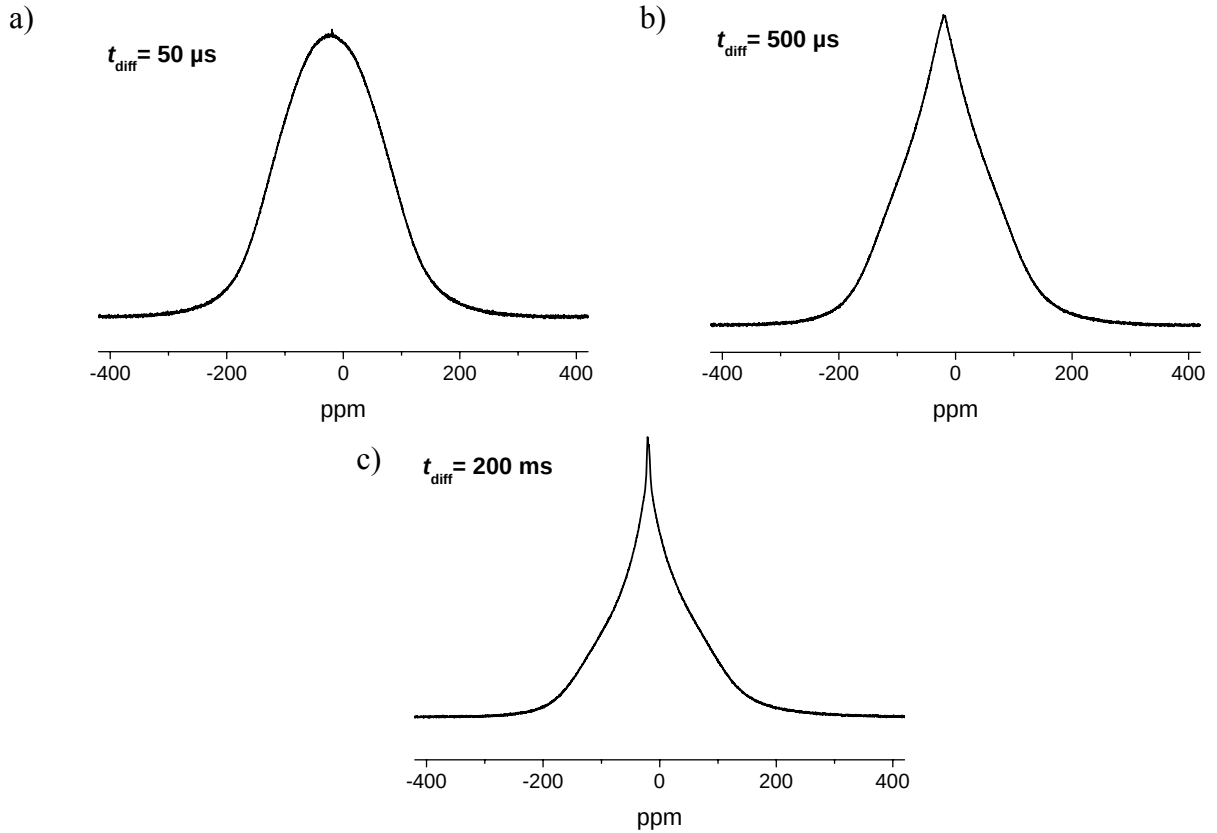


Fig. 4.15 Proton NMR spectra edited by the spin-diffusion experiment (Fig. 1) for spin-diffusion times: a) $t_d = 50 \mu s$, b) $t_d = 500 \mu s$, and c) $t_d = 200 ms$.

The decay and build-up spin-diffusion curves for iPP and iPP with different contents in PEOS are shown in Fig. 4.16. The thickness of the rigid and soft domains of the iPP/SiO₂ composite was determined by a fit of the signal integrals for these fractions as a function of the spin-diffusion time. For this purpose two-dimensional (2D) analytical solutions (cf. Eqs. 4.8 – 4.9) for the spin-diffusion equations were used. The values of the spin-diffusivities in the solution of the spin-diffusion equations for the rigid and soft fractions of the iPP/SiO₂ composites were taken from Fig. 4.14.

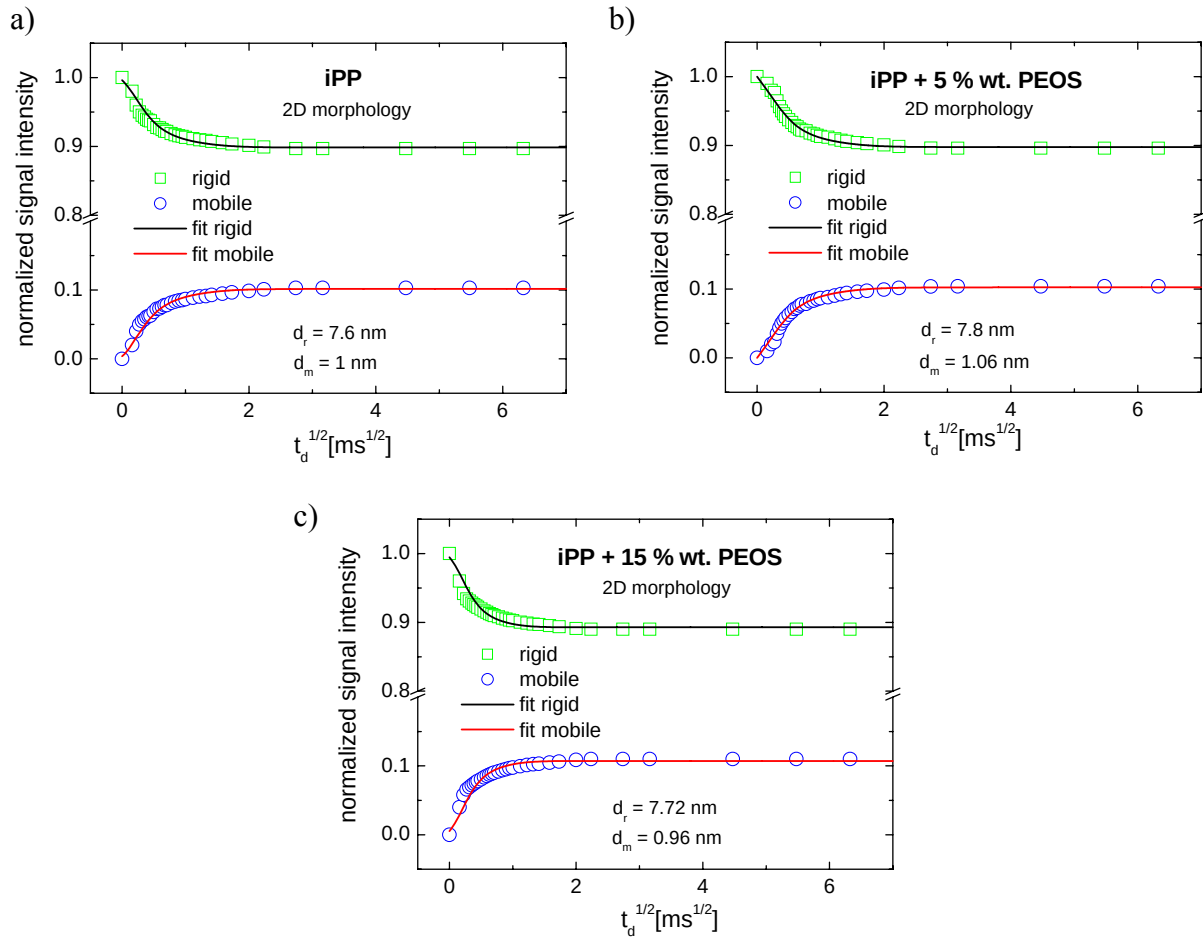


Fig. 4.16 Proton spin-diffusion decay and buildup curves for a) pure iPP, b) iPP with 5 wt.% PEOS, and c) iPP with 15 wt.% PEOS. The simulations of the spin-diffusion data are shown with continuous lines.

The long period $L_p = d_R + d_M$ of the iPP lamellae can be obtained from the experimentally determined values of d_R and d_M . The dependence of the domain thickness and the long period in iPP with different contents in PEOS is shown in Fig. 4.17. A small increase in the domain thickness is detected when the PAOS content increases from 0 wt.% to 20 wt.%. It should be noted, that the shape of the spin-diffusion curves could be affected by spin-lattice (T_1) relaxation. In the present study, the spin-diffusion process was completed at the

longest mixing time $t_d \approx 60$ ms, which is shorter than $T_1 \approx 120$ ms so that no T_1 correction of the spin-diffusion data was needed.

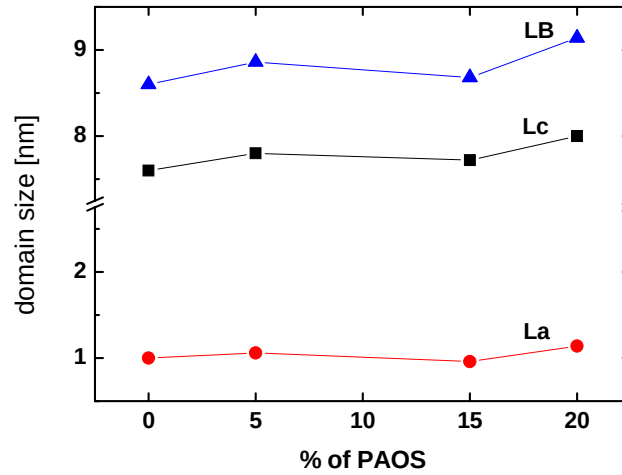


Fig. 4.17 Rigid and mobile domain thickness and long period for iPP with different content of PEOS.

Dynamic heterogeneity of iPP/SiO₂ composite at interface. The ¹H spin-diffusion experiment using a DQ filter allows us to measure the spatial evolution of the z-magnetization front by the spectral decomposition. At the beginning of the spin-diffusion experiment the magnetization is stored only in the rigid domain. For short spin-diffusion times the magnetization is present only in the rigid and interface domains. At longer diffusion times the z-magnetization front will reach the mobile region, where it spatially evolves until the thermodynamic quasi-equilibrium is reached.

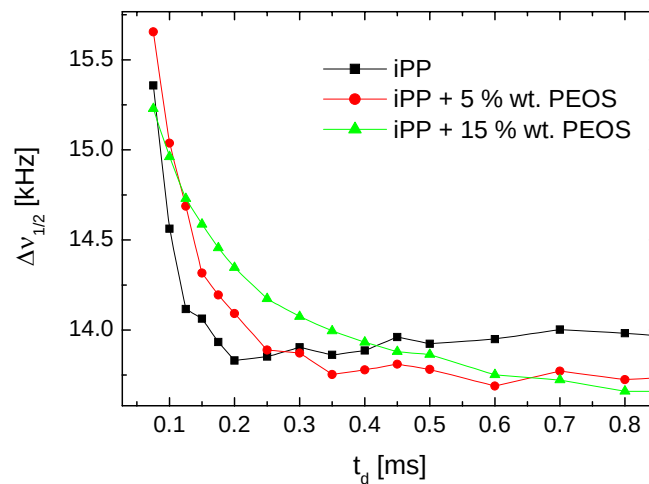


Fig. 4.18 Full line-width at the half intensity ($\Delta v_{1/2}$) of the interfacial component of the ¹H NMR spectrum for iPP with different content in PEOS as a function of spin-diffusion time t_d .

The interfacial region has a gradient in molecular mobility and therefore a monotonic change in the line-width at the half-intensity can be detected. At smaller spin-diffusion times

the experiment edits the part of the interface closer to the rigid region. For longer diffusion times the most mobile part of the interface connected to the mobile region will be edited. The gradual changes in the line-width at the half-intensity of the interface spectral component are shown in Fig. 4.18 for iPP and iPP with 5% and 15% wt. PEOS. The largest gradient in the molecular mobility is detected for the iPP sample. The chain mobility at the interface changes less steep for the PP/silica nanocomposite samples. The chain motion hindrance at the interface increases with PEOS content, as shown also in Fig. 4.11.

Small-angle X-ray scattering (SAXS). The SAXS measurements were done at *Institut de Chimie des Surfaces et Interfaces*, Mulhouse (France), under the supervision of Prof. Dr. Dimitri A. Ivanov. For all samples (oriented vertically) good orientation of the SAXS peaks was identified. The pure iPP film was found to be less oriented compared to the composites. At least two diffraction orders are present on the pattern of iPP+20 wt.% of PEOS (Fig. 4.19).

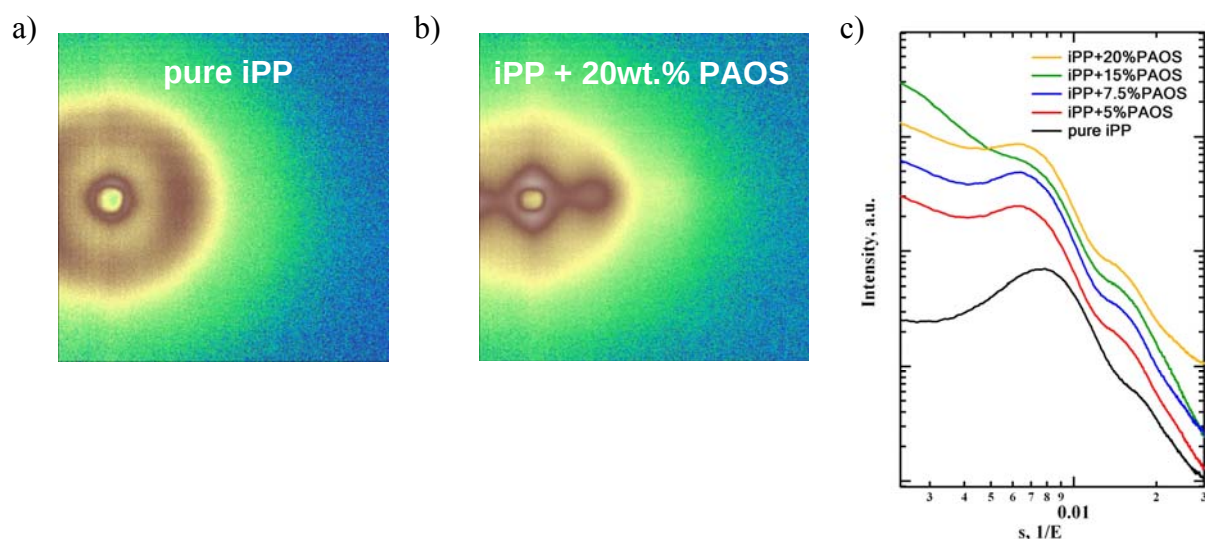


Fig. 4.19 SAXS patterns of a) pure iPP and b) iPP+20 wt.% PEOS samples. c) The 1D profiles integrated in the horizontal direction prove that the long period LB for the composites increases compared to the pure iPP.

Plotting the horizontal profiles taken from the SAXS patterns, one can see that for all composites the position of the SAXS peak does not change significantly with increasing the PEOS content. In contrast, the curve of iPP sample shows a shift of the peak to wider angle, indicating a decrease of the long period as compared to the composite samples. A detailed analysis using correlation and interface distribution functions numerically proved this hypothesis.

The domain sizes obtained by SAXS are presented in Fig. 4.20. An increase of crystal thickness (L_c) and long period (LB) for the composites compared to pure iPP can be

observed, while the amorphous thickness (La) remains the same for all samples. However, only small variations of the morphological parameters were found for all contents of PAOS. Probably, even a small amount of PEOS can play the role of a lubricant for the iPP chains, allowing them to organize more easily.

It is evident from Fig. 4.17 and Fig. 4.20 that the NMR and SAXS data are in a very good agreement, with a slight difference in the absolute values.

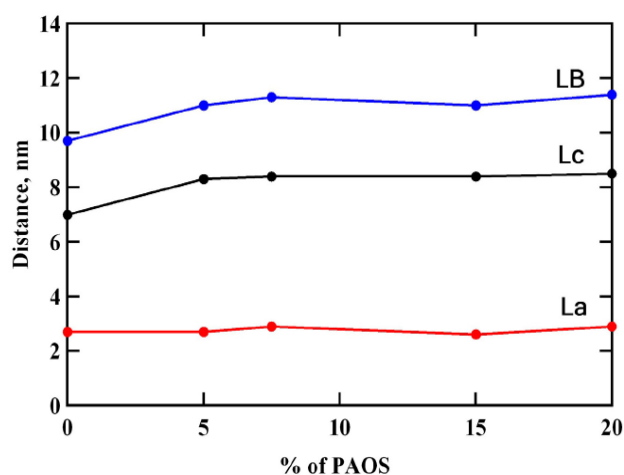


Fig. 4.20 Rigid and mobile domain sizes and long period for iPP and iPP/SiO₂ composites, as given by SAXS.

Differential scanning calorimetry measurements. Typical DSC curves of the PP/silica composites as well as pure PP are shown in Figure 4.21, and the DSC data are summarized in Table 4.6. The melting temperature of all the samples at the first and second heating runs was found to be identical. However, the crystallization temperature measured from cooling the melt with 10 K/min, as presented in Fig. 4.21, is increased for about 10 K by silica particle inclusion. This result shows that the *in situ* formed silica particles have a remarkable nucleation effect in the PP matrix. The crystallization temperature does not depend on the silica content. This can be understandable, since the saturation of nucleation efficiency takes place normally at concentration less than 1 wt% [Kri1, Jai2].

The crystalline fraction (X_c) of PP in the composite was determined from the DSC data. For any given samples, the crystalline fraction (X_c) can be calculated from the melting curve data in the following way:

$$X_c = \frac{\Delta H_f / F}{\Delta H_f^0}, \quad (4.10)$$

where ΔH_f is the melting enthalpy of the composite which is given by the area under the endotherm, and $\Delta H_f^0 \approx 207.1$ J/g is the melting enthalpy for 100% crystalline PP [Wun1].

The factor F is the actual weight percentage of PP contained in the samples, and it be calculated as $F \approx 1 - \text{SiO}_2\%$, where $\text{SiO}_2\%$ is the SiO_2 content in the PP/silica composites.

Table 4.6 DSC data for PP/silica composites at a heating and cooling rate of 10 K/min (subscripts: c – crystallization, m1 – first melting, m2 – second melting)

PEOS content (wt%)	T_c ($^{\circ}\text{C}$)	ΔH_c (J/g)	T_{m1} ($^{\circ}\text{C}$)	ΔH_{m1} (J/g)	Crystallinity of molded sample	T_{m2} ($^{\circ}\text{C}$)	ΔH_{m2} (J/g)	Crystallinity of melt-cooled sample
0	115.8	98.0	170.2	91.1	44.0%	167.3	101.6	49.1%
7.5	121.2	101.5	168.4	91.4	44.2%	166.1	106.8	51.6%
5	120.9	102.0	169.8	92.3	44.6%	166.0	107.1	51.7%
10	119.8	101.4	169.0	92.6	44.7%	165.4	107.2	51.8%
15	121.4	101.8	168.3	92.7	44.8%	166.2	107.4	51.9%
20	120.0	103.1	169.7	103.2	49.8%	165.7	109.6	53.0%

PP is a semi-crystalline polymer, its physical and mechanical properties are greatly influenced by the degree of crystallinity and the orientation distribution of the crystalline volume portion. The crystalline fractions of all prepared samples obtained from the first and second heating runs are shown in Table 4.6. As can be seen, the general tendency is an increase of crystallinity of PP by increasing silica loading. This is somehow in contradiction with the solid state NMR data, which show a slight decrease of the crystalline fraction (Fig. 4.10). This difference can be explained by the effect of the rigid fraction of the interface, which is not taken into account in the analysis of the DSC data.

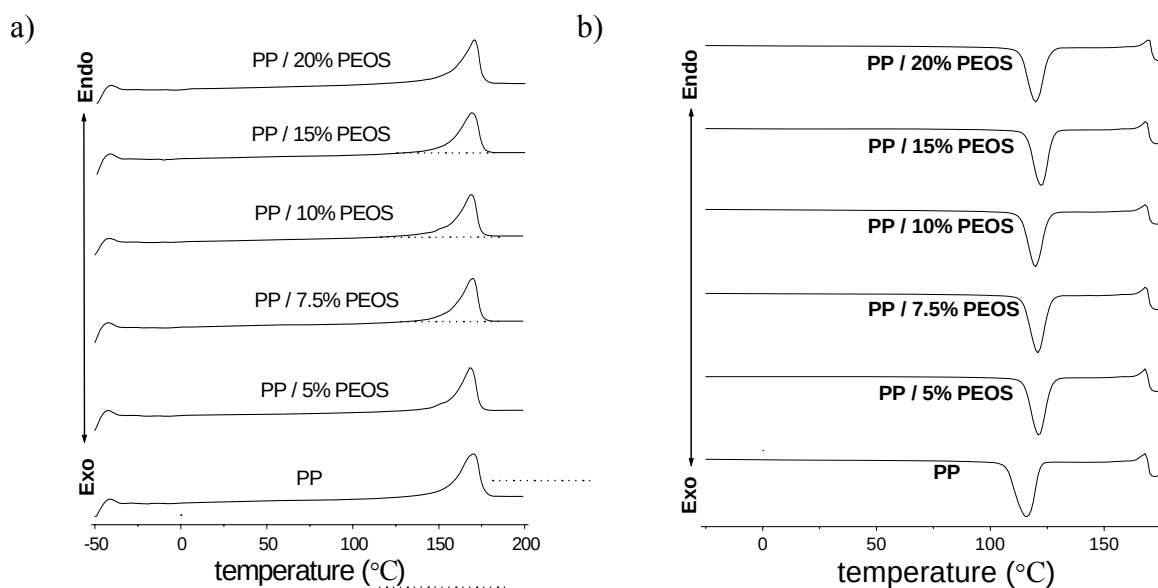


Fig. 4.21 DSC thermograms of PP/silica composites. a) First heating; b) Cooling.

Thermogravimetric analysis (TGA). TGA curves of PP and PP/silica samples are shown in Figure 4.22. First of all, the char formation of PP/silica is higher than that for pure PP, and it is increased with the PEOS content. The residual mass after pyrolysis at 600° C agrees quite well with the theoretical SiO₂ content in these PP/silica composites (Table 4.1). At the same time, as shown in Fig. 4.22, the degradation temperature of the composites is higher than that of pure PP, and is again increasing with increasing PEOS loading. It can be concluded that the PP/silica composites prepared by *in situ* sol-gel technology have improved thermal properties.

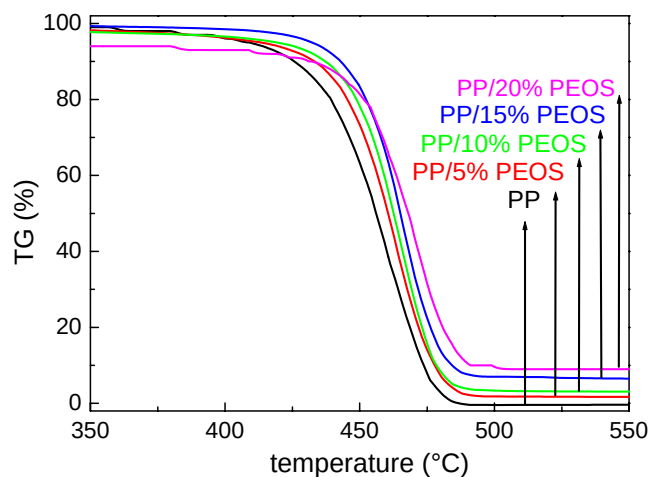


Fig. 4.22 TGA curves of PP and PP/silica composites.

Mechanical tests. The mechanical properties of the composite materials were evaluated by tensile test. The dependence of Young's modulus on silica content is shown in Fig.4.23. In general, the *in situ* generated silica particles do not influence significantly the Young's modulus of the composites. At low silica content (2-6 wt.%), the PP/silica composites exhibit slightly smaller Young's modulus in comparison with that of pure PP. This decrease is possibly related to the low degree of conversion, which was proved by solid state NMR measurement (Table 2). At high silica loading, the PP/silica composites and pure PP have similar Young's modulus. It might be the result of the interplay of the crystallinity and filler-filler interaction.

The stain-stress curves of the PP/silica and PP samples are presented in Fig. 4.24, and they show that all composites prepared in this work show the typical feature of ductile materials. It is interesting to note that the elongation-at-break of the composites with up to 6 wt % of silica inclusion is not affected by the *in situ* formed silica particles. When the silica content reaches 8.1 wt%, the elongation-at-break value decreases remarkably from 1100 % to 800 %, possibly because of the formation of large silica particles.

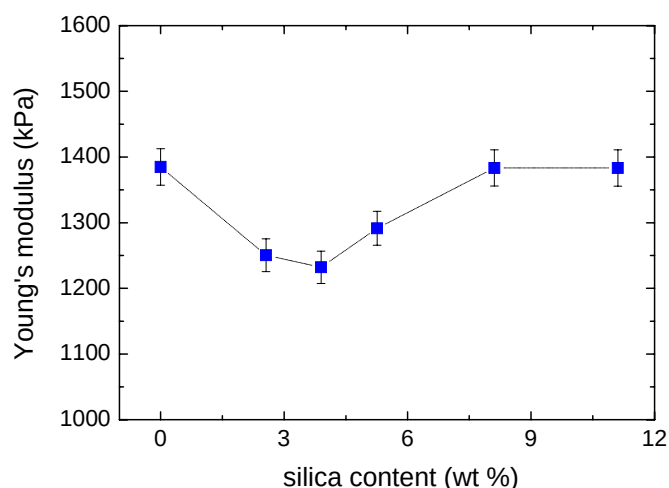


Fig. 4.23 Young's modulus *versus* silica content for PP/silica composites.

The slope of the strain-stress curves at high strains (400 % - 1200 % range) can be taken as a measure for the strain hardening modulus. The decrease of the strain hardening modulus was observed for the PP/silica composites during stretching at high strains (Fig. 4.24). This should be the result of the less entangled, more mobile amorphous phase caused by silica inclusion [Sch2].

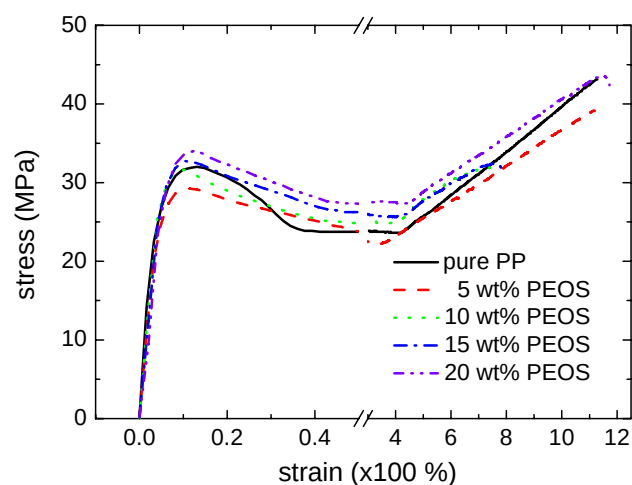


Fig. 4.24 Strain-stress curves of PP/silica composites.

4.4 Conclusions

A continuous procedure for the preparation of polymer/inorganic composites by means of *in situ* sol-gel technology using hyperbranched polyethoxysiloxane (PEOS) has been investigated. Due to the non-volatility of PEOS, the SiO₂ content of the composites could easily be controlled. With low PEOS loading this procedure yielded PP/silica composites with

particle diameter less than 100 nm. The particle size increased with the increase of the PEOS amount blended with PP. Nevertheless, the particles were found to be homogeneously dispersed in the polymer matrix. PP/silica composites prepared by *in situ* sol-gel technology showed improved thermal properties, but almost not affected mechanical properties as compared with pure PP.

Proton wide-line NMR spectroscopy, ^1H DQ buildup curves, and ^1H spin-diffusion NMR were used for microscopic and mesoscopic characterization of the iPP/SiO₂ hybrid system. At the microscopic scale, the presence of hyperbranched polyethoxysiloxane hinders the chain motions in all three domains of iPP.

On the mesoscopic scale, the amount of rigid, interfacial, and mobile fractions of iPP does not change essentially with the PEOS content in the range from 0 to 20 wt.%. The packing of the proton network is characterized by the residual van Vleck second moment that slightly increase by the presence of silica particles. The long period, and the rigid and amorphous domain sizes were measured by ^1H spin-diffusion NMR in the approximation of two-dimensional and two-phase morphology. The rigid and amorphous domain sizes increase slightly in the presence of silica particles in agreement with the results from SAXS.

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5 Morphology and chain dynamics of UHMWPE by ^1H , ^{13}C and ^{129}Xe NMR spectroscopy and relaxometry

5.1 Introduction

Fibers or tapes with superior modulus and strength can be prepared by the so called gel spinning/drawing process from ultrahigh molecular weight polyethylene (UHMWPE) [Lem1, Ana1, Mat1, Mat2]. The process allows the conversion of chain folded lamellar crystals into highly oriented chain extended structures and the fiber properties approach values as given by the theoretical limitation of the strength of a carbon-carbon bond. At present, UHMWPE fibers have been prepared with moduli up to 170 GPa and strength up to 4 GPa [Kir1]. However, for analyzing and predicting the physical performance of these mechanically deformed and oriented semicrystalline polymers, a qualitative and quantitative understanding of their component microstructure is crucial.

The morphological structure of drawn semi-crystalline polymers is considerably more complex than can be described by a simple two-phase model [Pet1, Lin1, His1]. When UHMWPE is uniaxially deformed and necked, the original spherulitic arrangement of lamellar crystallites is dramatically transformed into a highly oriented, fibrillar microstructure with molecular chains that are mostly parallel to the draw axis. It is generally agreed that the crystalline lamellae are broken into small “mosaic” blocks during necking. Hence, to account for the mechanical integrity and increased strength along the draw direction, various morphological structures such as tie molecules [Pet1, Pet2, Pet3] and inter-crystalline bridges [Gib1] have been invoked and incorporated into the classical two-phase model, yielding more intricate representations of the anisotropic morphology of drawn and oriented polyethylene.

Polyethylene fibers have been rather extensively studied by solid-state NMR [Hyo1, Kaj1, Tzo1, Tzo2, Che1, Hu1, Hu2], which provided valuable information about the amount of orthorhombic and monoclinic phases, disordered all-trans interfacial layer and amorphous phase, the size of crystalline and amorphous domains, the orientation of chains in these phases, the frequency of 180° chain flips in the crystalline phase, molecular mobility, or orthorhombic-to-hexagonal phase transition for constrained PE fibres. However, results of

these studies are not well known at DSM Dyneema[®] and hardly any NMR studies of UHMWPE fibers were performed at DSM Research in the past. One of these is the deuterium-NMR study done on deuterated, gel-drawn ultrahigh molecular weight polyethylene tapes in order to obtain information about the orientational distribution and the molecular mobility [Möll]. An increase of the spin-lattice relaxation time by about an order of magnitude ($T_1 > 200$ s) was observed in comparison to melt crystallized polyethylene indicating high perfection of the fibrillar crystallites. Beside the ^2H -NMR resonance of a highly ordered rigid component (orthorhombic or monoclinic fibrillar crystallites), a little oriented, highly mobile component was observed, whose fraction can be appraised between 5 and 10% and that can be assigned to constrained non-crystalline chain segments. In addition to these clearly separated components, it has been demonstrated that a minor part of the chain segments are highly oriented but also of considerable mobility. Variations in the line shape compared to the rigid oriented chains could be explained by a dynamic equilibrium of *all-trans* conformations and $<2\%$ *gauche* conformations in extended chain segments. Saturation - spin echo pulse experiments showed a continuous and smooth transition in the T_1 time and the resonance line of the oriented components, showing that the oriented mobile segments are part of the crystalline structure or at least directly linked to the crystallites. On the other hand, the very long T_1 times observed for the rigid component indicate a very high degree of perfection of the fibrillar crystallites. Thus, it appears that the mobile oriented chain segments are concentrated in small areas inside the fibrillar crystallites or which are directly attached to them. So the oriented mobile segments may be reasonably assigned to tie molecules between highly ordered crystal domains or areas of the crystallites in which trapped conformational defects are concentrated.

The aim of the study presented in this chapter is to try to fill the existing knowledge gap regarding a detailed molecular understanding of DSM Dyneema[®] UHMWPE fibers. This can provide afterwards the necessary information about a delicate optimization of the fiber structure, which can be translated in the end into an improved performance of these fibers.

Using a series of drawn UHMWPE experimental and commercial fibers, the phase composition and chain dynamics is investigated by means of wideline ^1H NMR, domain sizes of different phases are calculated, the chain ordering and packing is studied using the M_2 and M_4 proton Van Vleck moments, the chain mobility and local methylene group motions are estimated through wideline separation (WISE) NMR, and the intermediate fraction is investigated using ^{13}C NMR. The voids sizes (free volume) inside the UHMWPE matrix are determined by means of thermally polarized ^{129}Xe NMR spectroscopy.

5.2 Experimental

Samples. A series of drawn ultra high molecular weight polyethylene (UHMWPE) fibers with different tensile strength (σ_{TS}) values (Table 5.1), in the 1.56 GPa - 4.8 GPa range, was provided by DSM Dyneema[®]. These are experimental samples produced using the patented *gel spinning* DSM method. Tensile strength is defined as the maximum load that a material can support without fracture when being stretched, divided by the original cross-sectional area of the material. When stresses less than the tensile strength are removed, a material returns either completely or partially to its original shape and size. As the stress reaches the value of the tensile strength, however, a material, if ductile, that has already begun to flow plastically rapidly forms a constricted region called a neck, where it then fractures.

Table 5.1 Tensile strength values of Dyneema[®] fibers investigated

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
σ_{TS} [GPa]	1.56	2.5	2.9	3.3	3.9	4.6	4.8

¹H NMR spectroscopy. Proton NMR spectra were recorded with a Bruker DSX 500 NMR spectrometer ($B_0 = 11.75$ T) at a ¹H resonance frequency of 500.44 MHz, using a single 90° radio-frequency excitation pulse of 5 μ s length at 6 dB power attenuation. The samples were randomly packed in a 4 mm ZrO₂ rotor and measured under both static and 10 kHz magic-angle spinning (MAS) conditions, at ambient temperature, 50°C and 70° C.

¹³C NMR spectroscopy by ¹H-¹³C cross-polarization under MAS. The ¹³C solid-state NMR experiments were conducted using a Bruker DSX 500 spectrometer ($B_0 = 11.75$ T) at a ¹³C resonance frequency of 125.84 MHz and a ¹H resonance frequency of 500.44 MHz. Measurements were made at ambient temperature ($T = 295$ K) under moderate magic angle sample spinning (MAS) of 5 kHz. For all experiments, a double-resonance Bruker MAS NMR probehead and 4 mm diameter zirconia rotors were used to hold the samples.

The whole set of measurements was done in such a way that the fibers were cut into pieces of 1.5 cm length and introduced in the rotor, aligned with the rotor axis (Fig. 5.1). The rotor inside the MAS NMR probehead makes an angle $\theta = 54.7^\circ$ (the so called *magic angle*) with respect to the B_0 magnetic field.



Fig. 5.1 The fibers were partially aligned along the rotor axis; the 4 mm diameter rotor is oriented inside the spectrometer's NMR probehead along the magic angle $\theta = 54.7^\circ$ with respect to the B_0 magnetic field.

The standard cross-polarization (CP) measurements under MAS [Pin1, Dem2, Har1], whose pulse sequence is described in Fig. 1.2, utilized a 5 kHz spinning speed, a ^1H 90° pulse length of $8.4\ \mu\text{s}$ at 7 dB attenuation, and a contact time of 1.5 ms on both ^1H and ^{13}C channels, with a power attenuation of 7 dB and 12 dB respectively, allowing the heteronuclear cross-polarization transfer. The time dependent signal of ^{13}C was recorded under high power decoupling using the broadband pulse sequence TPPM20 (two-pulse phase modulation), consisting of a train of 180° pulses on the ^1H channel, with a phase difference of 20° between the subsequent pulses [Tha1]. The power attenuation used for the 180° decoupling pulses was 4 dB and the length of the pulses was $14\ \mu\text{s}$. A time domain of 8192 points and a $10\ \mu\text{s}$ dwell time between two consecutive points were used for the digital sampling of the recorded signal, giving a total acquisition time of 81.92 ms (i.e. the time needed for recording the ^{13}C complete FID). The dead time of the spectrometer is on the order of $5.5\ \mu\text{s}$.

^{13}C - ^1H WISE. For the two-dimensional (2D) wide-line separation (WISE) NMR experiments, as an element of originality, a very short CP contact pulse of only $50\ \mu\text{s}$ was used in order to minimize the ^1H spin-diffusion during this polarization transfer time. The pulse sequence used for these experiments is displayed in Fig. 1.3. It starts with a 90° radio-frequency pulse of $7\ \mu\text{s}$ length at 12 dB power attenuation on the ^{13}C channel followed, after a short delay of $30\ \mu\text{s}$, by a 90° pulse of $8.4\ \mu\text{s}$ at 7dB power attenuation on the proton channel. Coming next is an incremented proton evolution period (t_1) which starts with the initial value of $1\ \mu\text{s}$ and is increased afterwards in 128 steps, always with the same value of $1\ \mu\text{s}$. By means of Hartmann-Hahn cross polarization from protons to carbons, the proton magnetization at the end of the evolution period transformed into amplitude modulation of the ^{13}C signal, which is probed in the t_2 domain of the experiment, in the presence of a ^1H - ^{13}C heteronuclear dipolar decoupling. The contact pulse (CP) has a length of $50\ \mu\text{s}$ on both ^1H and ^{13}C channels, using a

power attenuation of 7 dB and 12 dB respectively. The ^{13}C free induction decay (FID) is detected under high power decoupling using the TPPM20 pulse sequence.

To eliminate the effects of orientation in the material, the samples were artificially made isotropic by carefully cutting the fibers into pieces about 2 mm in length along the draw direction. This size was considered small enough for the sample pieces to be randomly packed in the 4 mm diameter rotor, but large enough that the concentration of stress-induced microstructures like monoclinic crystals was not significantly enhanced due to cutting (Fig. 5.2).



Fig. 5.2 Preparation of the Dyneema® samples used for the $^{13}\text{C} - ^1\text{H}$ WISE experiments.

^{13}C $T_{1,C}$ filter. Utilizing an “inverse $T_{1,C}$ filter” it is possible to selectively observe the signals of short ^{13}C T_1 magnetization with good CP efficiency. The basic pulse sequence for the inverse $T_{1,C}$ filter (Fig. 5.3) is the same as for a traditional ^{13}C T_1 filter [Mow1]. An X-second inverse $T_{1,C}$ filtered spectrum is obtained as the (unscaled) difference between an X-second $T_{1,C}$ filtered spectrum and a reference spectrum obtained with the same pulse program and a very short (1 ms) relaxation delay.

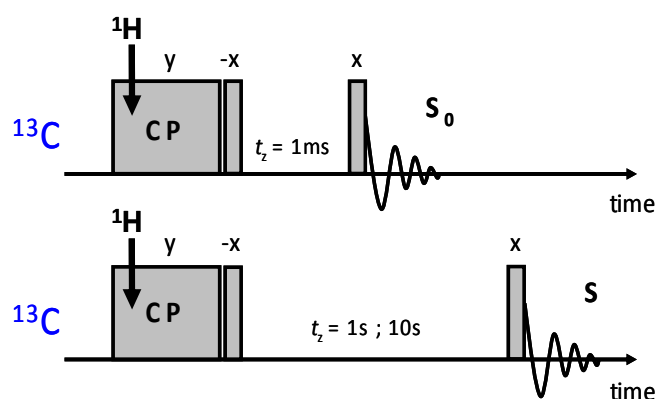


Fig. 5.3 Pulse sequence of the “inverse $T_{1,C}$ filter” experiment. Utilizing the $T_{1,C}$ filter pulse sequence of Torchia [Tor1], with variable $T_{1,C}$ filter delay time t_z , an X-second inverse $T_{1,C}$ filtered spectrum (ΔS) is obtained as the unscaled difference between an X-s $T_{1,C}$ filtered spectrum (S , where $t_z = X$ s) and a reference spectrum (S_0 , where $t_{z,\min} = 1$ ms) acquired with the same number of scans.

Quantitatively, the spectral intensity after a $T_{1,C}$ filter of duration t_z can be written as the sum of the cross-polarization signals $S_{n,CP}(\omega)$ of the different components, each weighted by $\exp(-t_z/T_{1,n})$, where $T_{1,n}$ is the ^{13}C longitudinal relaxation time of the n th component [Mow1]. The difference signal ($\Delta S = S - S_0$ in Fig.5.3) is then:

$$S_{inv,fil}(\omega, t_z) = \sum_n e^{-0/T_{1,n}} S_{n,CP}(\omega) - \sum_n e^{-t_z/T_{1,n}} S_{n,CP}(\omega) = \sum_n (1 - e^{-t_z/T_{1,n}}) S_{n,CP}(\omega) \quad (5.1)$$

If the relaxation time of component n_0 is long, $T_{1,n_0} \gg t_z$, the signal of that component is canceled, while the signals of other components with short relaxation times are retained. The inverse $T_{1,C}$ filtered spectrum is like a one-pulse spectrum with a recycle delay of duration t_z , where the signal of each specific chemical group is multiplied with its CP efficiency. In an extension of this concept, differences between spectra for two intermediate times t_{za} and t_{zb} can be taken. This eliminates the signals of components with short $T_1 \ll t_{za} < t_{zb}$ as well as long $T_1 \gg t_{zb} > t_{za}$, which enables selection and isolation of the signals of components with intermediate $T_{1,C}$ relaxation times.

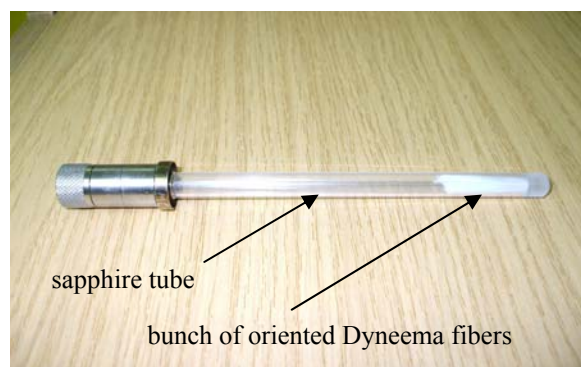


Fig. 5.4 High-pressure resistant sapphire tube with the partially oriented UHMWPE fibers used for the ^{129}Xe NMR measurements.

^{129}Xe NMR spectroscopy. Thermally polarized ^{129}Xe NMR spectra were recorded with a Bruker DMX 300 NMR spectrometer ($B_0 = 7\text{ T}$), operating at 300 MHz ^1H resonance frequency and 83.4 MHz ^{129}Xe resonance frequency. The measurements were done using a micro-imaging probehead and a 10 mm diameter ^{129}Xe resonator. A home-built sapphire tube able to sustain a maximum gas pressure of 30 bar was used to upload the drawn UHMWPE fibers with ^{129}Xe . Partially oriented fibers of about 2.5 cm length were introduced into the tube (Fig. 5.4) and kept in a 20 bar pressure ^{129}Xe atmosphere for one week before the NMR measurements. In all measurements the recycle delay was set to 120 s due to the very long T_1 relaxation time of ^{129}Xe . Choosing 1024 scans, one experiment took about 34 hours. The measurements were done at room temperature. The dwell time was 10 μs and the length of the

90° radio-frequency pulse was 13 μ s at a power attenuation of -6 dB (low power regime). The dead time of the spectrometer was about 5.5 μ s.

5.3 Results and discussion

5.3.1 Phase composition and chain dynamics by ^1H NMR

Performing the whole set of measurements at room temperature and under static conditions, the ^1H NMR spectra were recorded for the entire series of samples. A comparison between the spectra corresponding to Dyneema[®] fiber with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa is shown in Fig. 5.5.

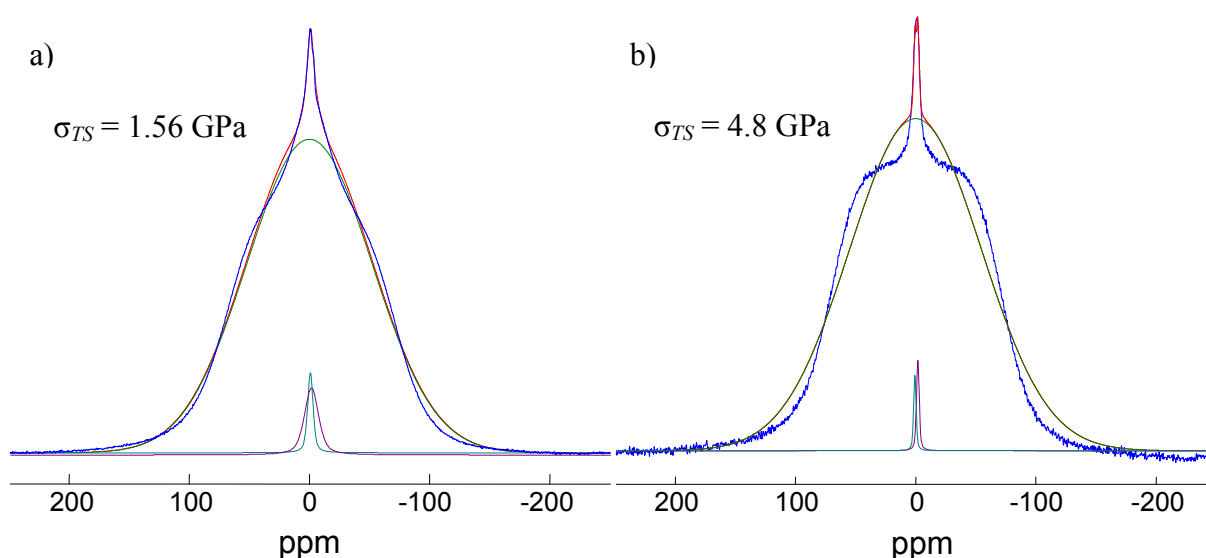


Fig. 5.5 Proton NMR spectrum of Dyneema[®] fiber with a) $\sigma_{TS} = 1.56$ GPa and b) $\sigma_{TS} = 4.8$ GPa, and the numerical spectral deconvolution based on a 3-component model, using the "dmfit program" [Mas1]. The blue line corresponds to the real spectrum.

For both spectra a partially successful deconvolution was performed with "dmfit program" [Mas1]. Three components were detected corresponding to rigid, interface and highly mobile phases. The strong dipolar couplings in the crystalline domains lead to an Abragam free induction decay (FID) [Abr1]. Unfortunately at this stage all commercially available deconvolution programs are able to use only Gaussian functions to simulate the rigid component. And it is evident from the above figures that the Gaussian just approximates description the real spectrum. In order to improve the deconvolution, a new procedure based

on the numerical fit of the NMR spectra using the Fourier transformation (FT) of the Abragam function had to be developed.

Unfortunately, the FT (Mathcad) of the Abragam function:

$$G(t) = A \exp(-at^2) \frac{\sin(bt)}{bt} \quad (5.2)$$

has no analytic form, i.e.:

$$G(\omega) = \frac{\pi A}{2b} \left[\operatorname{erf} \left[\frac{-\omega + b}{2\sqrt{a}} \right] + \operatorname{erf} \left[\frac{+\omega + b}{2\sqrt{a}} \right] \right] \quad (5.3)$$

where $\operatorname{erf}(x)$ is the error function integral defined only in a numeric fashion. Therefore, a specialized numerical program had to be written to fit such spectra. Such a procedure is shortly described below.

The functions used in the numerical fit program written in C++ are:

Gauss (for the interfacial fraction)

$$G_s(x) = A_G \exp \left\{ -\ln(2) \left(\frac{x - x_G}{\sigma_G} \right)^2 \right\} \quad (5.4)$$

where $\ln(2)$ was introduced because in this way the σ_G is the half-width at half-height.

Lorentz (for the mobile amorphous fraction)

$$L(x) = \frac{A_L}{1 + \left(\frac{x - x_L}{\sigma_L} \right)^2} \quad (5.5)$$

where σ_L is the half-width at half-height and

Abragam (for the rigid fraction)

$$Ab(t) = A_{abr} \exp \left\{ -\frac{a^2}{2} t^2 \right\} \frac{\sin(bt)}{bt}. \quad (5.6)$$

For a good fit one has to consider only the real part of the Fourier transform, i.e. $Ab(x) = \operatorname{REAL}\{\operatorname{TF}[Ab(t)]\}$. The second (M_2) and the fourth (M_4) van Vleck moments [McB1] that carry information about chain packing are directly related to the parameters a and b of the Abragam function, i.e.:

$$M_2 = a^2 + \frac{1}{3} b^2, \quad (5.7)$$

$$M_4 = 3a^4 + 2a^2 a^2 + \frac{1}{5} b^4. \quad (5.8)$$

The general flow diagram of the C++ numerical program is presented below (Fig. 5.6). It is essentially based on the iterative Levenberg-Marquardt algorithm that minimizes the deviations from the calculated and the experimental spectrum.

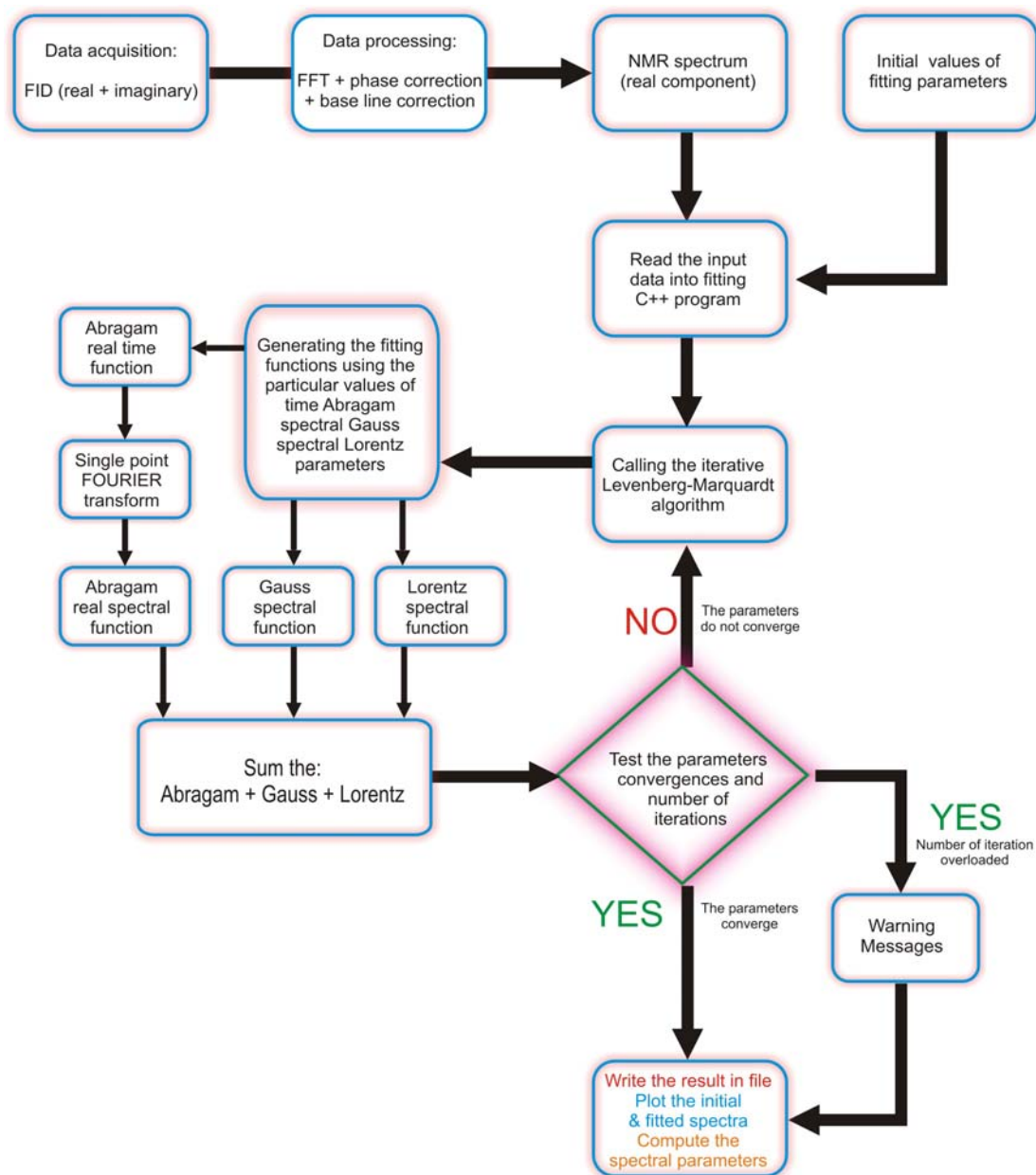


Fig. 5.6 The general flow diagram of the C++ numerical program developed in order to be able to accurately decompose the ^1H spectra of UHMWPE Dyneema[®] fibers.

A first attempt to deconvolute the ^1H spectrum of fiber with $\sigma_{TS} = 1.56$ GPa with the new program is shown in Fig. 5.7. This time it can be seen that the real spectrum is more accurately fitted. The optimization of the program is still in progress, so some fitting errors are still present. But nevertheless the deconvolution of the ^1H wideline NMR spectra of the

whole UHMWPE fibers series, in order to investigate the phase composition as a function of σ_{TS} , has been done and the results are presented in Fig. 5.8.

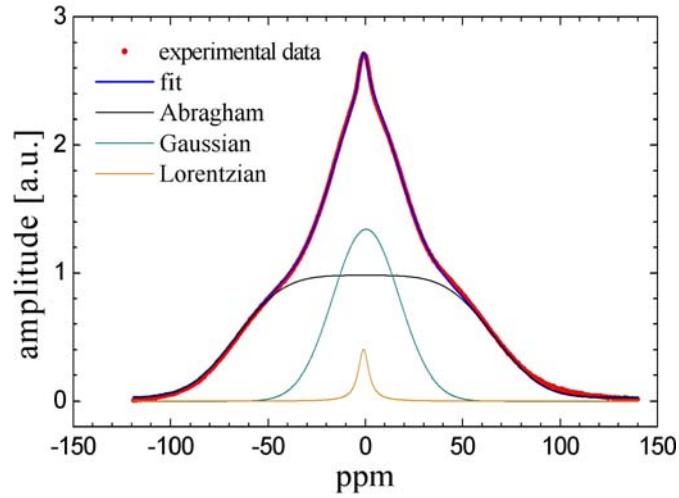


Fig. 5.7 Example of decomposition of ^1H spectrum of the fiber with $\sigma_{TS} = 1.56$ GPa using the new developed C++ program.

From this diagram one can conclude that the rigid fraction increases from 97% to 99% as a result of drawing and remains practically constant for samples with $\sigma_{TS} \geq 2.9$ GPa. A jump is present for the sample with $\sigma_{TS} = 2.5$ GPa, probably due to a change in the processing conditions. An increase in the concentration of the interface and the mobile fractions is present for this sample. Besides the rigid component, an interface and a highly mobile fraction are detected for the samples less drawn. For larger values of σ_{TS} one can approximate that only a single fraction is present, so a kind of “collapse” of the interface with the mobile phase takes place for $\sigma_{TS} \geq 2.9$ GPa, the concentration of these two components being less than 1%.

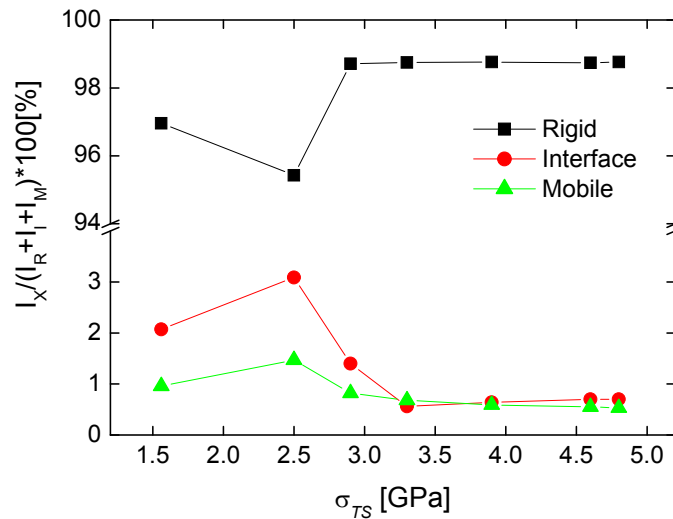


Fig. 5.8 Relative phase composition of Dyneema® UHMWPE fibers as a function of σ_{TS} .

In order to improve the accuracy of the analysis of the phase composition, the dependence of the ^1H NMR spectra on fiber orientation and temperature have to be investigated. The difference between oriented and non-oriented Dyneema[®] fiber with $\sigma_{TS} = 4.8$ GPa is shown in Fig. 5.9 and, as one can see, it is substantial. Therefore it is recommended to perform these measurements on non-oriented samples to avoid the difficulties related to a good fiber orientation.

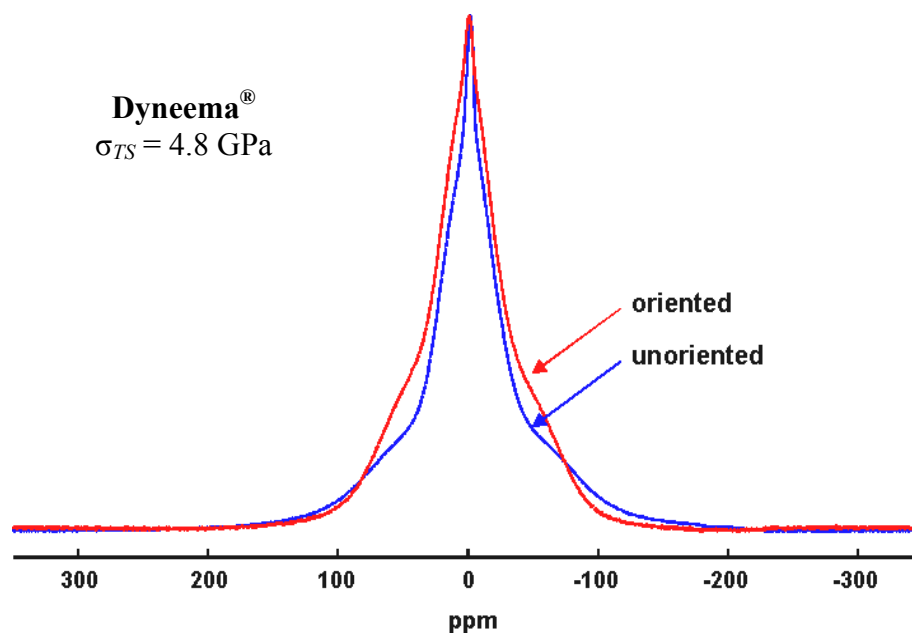


Fig. 5.9 Proton NMR spectra of partially oriented and non-oriented Dyneema[®] fiber with $\sigma_{TS} = 4.8$ GPa.

A way to enhance the contrast between the polymer phases in time- and frequency domain data is to perform the measurements at elevated temperatures. The ^1H NMR spectrum of Dyneema[®] sample with $\sigma_{TS} = 4.8$ GPa was recorded at three different temperatures (25°C,

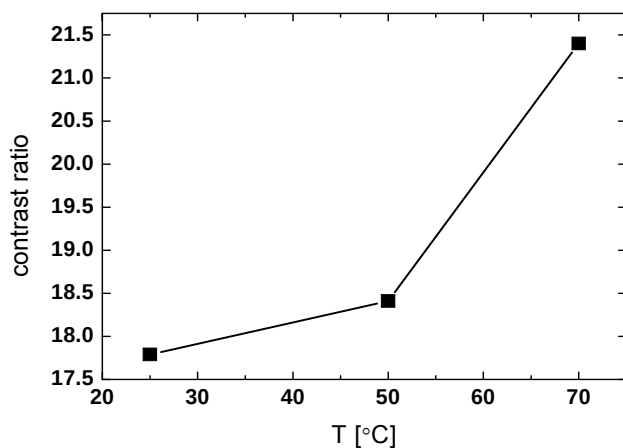


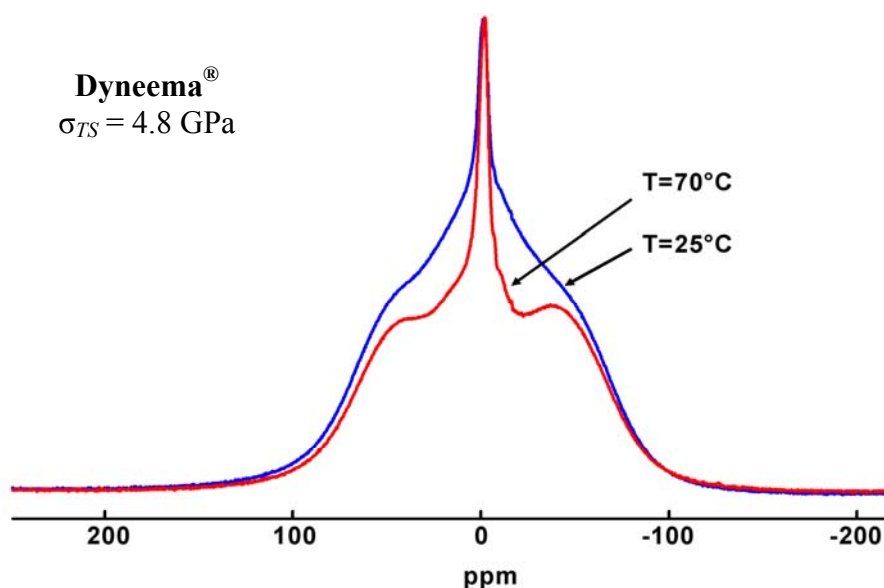
Fig. 5.10 Contrast ratio as a function of temperature.

50°C and 70°C) and decomposed into two components (rigid and mobile) using the “dmfit” deconvolution program, and the linewidth at half-height of each component was measured (Table 5.2). Calculating the *contrast ratio* (the ratio of the rigid-fraction linewidth and the mobile-fraction linewidth) it is obvious that it increases with increasing temperature (Fig. 5.10).

Table 5.2 The changes in phase composition and contrast ratio with temperature

Temperature [°C]	Phase Fraction [%]		Linewidth [Hz]		Contrast ratio
	rigid	mobile	rigid	mobile	
25	95.8	4.2	56352	3167	56352 / 3167 = 17.79
50	94.5	5.5	57937	3146	57937 / 3146 = 18.41
70	93.6	6.4	60132	2810	60132 / 2810 = 21.40

The effect of temperature on the shape of the spectrum for the Dyneema[®] sample with $\sigma_{TS} = 4.8$ GPa is shown in Fig. 5.11, where two ^1H NMR spectra, recorded at room temperature and at 70°C respectively, are superimposed.

Fig. 5.11 The enhanced contrast induced in ^1H NMR spectra by increasing the temperature.

The presence of some chemical “impurities” was detected in the Dyneema[®] fibers in a very simple manner, by recording a ^1H NMR spectrum under fast MAS of 10 kHz. This is shown in Fig. 5.12. At this stage we cannot make a clear assignment of the lines. Nevertheless, it is clear that both narrow lines correspond to chemical species with reduced molecular mobility, a fact proved by the presence of the spinning sidebands (weak signals appearing on top of the broad spectrum).

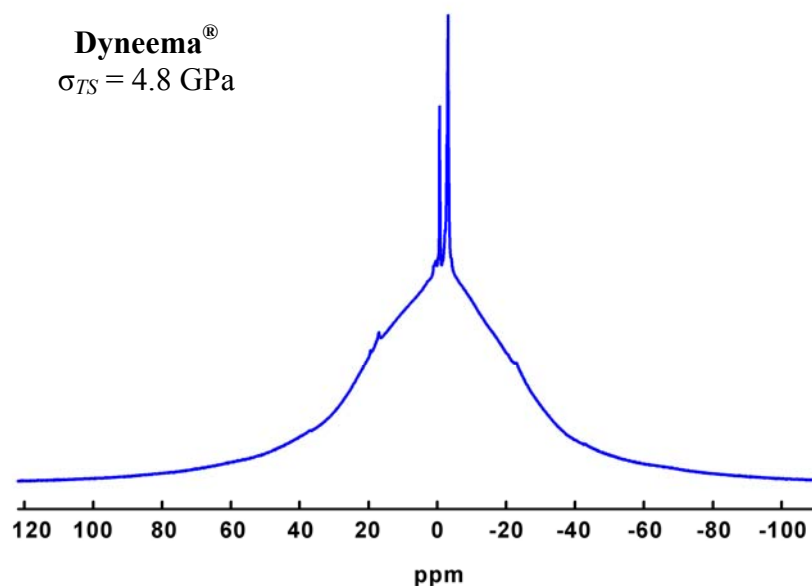


Fig. 5.12 Proton NMR spectrum of Dyneema[®] fiber with $\sigma_{TS} = 4.8$ GPa under fast MAS at 10 kHz. Two sharp signals can be observed in the middle of the spectrum. They are likely to correspond to some remaining chemical “impurities” from the processing stage of the fibers.

A simple NMR method that can be used to study the effect of drawing upon the chain mobility is given by the ^1H linewidth at half spectral intensity $\Delta\nu_{1/2}$. This quantity can be measured for each of the phases in the morphology of UHMWPE Dyneema[®] fibers, having their ^1H NMR spectra already deconvolved (Fig. 5.13). The rigid domains show a decrease in the chain mobility (i.e. an increase in $\Delta\nu_{1/2}$) as a function of tensile strength. The opposite behaviour is evidenced for the interface and the mobile regions. Moreover, for $\sigma_{TS} \geq 2.9$ GPa samples, these two phases cannot be differentiated. The linewidth is close to 1 kHz, being similar to the behaviour of polymer chains in elastomer systems.

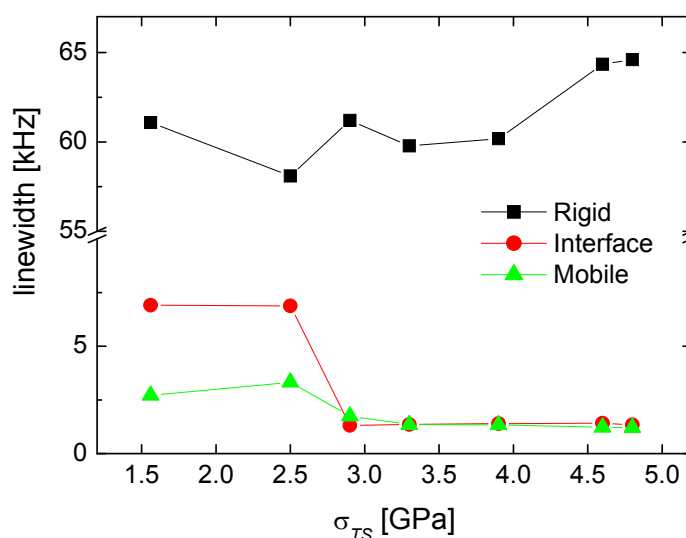


Fig. 5.13 The dependence of $\Delta\nu_{1/2}$ on tensile strength for Dyneema[®] fibers.

Because the mobile fraction of Dyneema[®] fibers could be associated with the presence of voids inside the structure of these materials, a method to detect only this specific component was developed. In this way the spectral deconvolution or the fits of the FID are avoided. The method is based on a delayed acquisition (DAQ), as shown in Fig. 5.14a. A typical NMR spectrum obtained using this method is presented in Fig. 5.14b. The delay time is $t_{AQ} = 50 \mu s$.

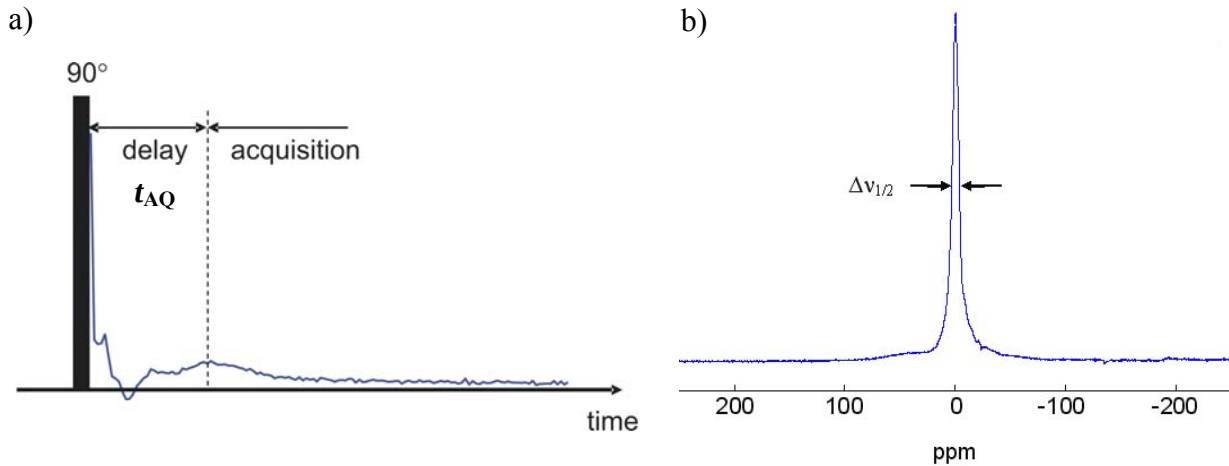


Fig. 5.14 a) The DAQ method used to select only the highly mobile component for our series of drawn UHMWPE fibers. The dark-blue line represents a typical FID recorded for the Dyneema[®] fiber with $\sigma_{TS} = 1.56$ GPa. b) Proton NMR spectrum corresponding to the highly mobile phase, selected using the DAQ method ($AQ = 50 \mu s$) for the Dyneema[®] fiber with $\sigma_{TS} = 1.56$ GPa.

The dependence of $\Delta\nu_{1/2}$ on the tensile strength is shown in Fig. 5.15. No systematic dependence on σ_{TS} is detected, due probably also to the low signal-to-noise ratio of the time-domain data and to the difficulty in doing the base line correction. So it can be concluded that the voids do not essentially affect the segmental dynamics of highly mobile polymer chains, irrespective of σ_{TS} value.

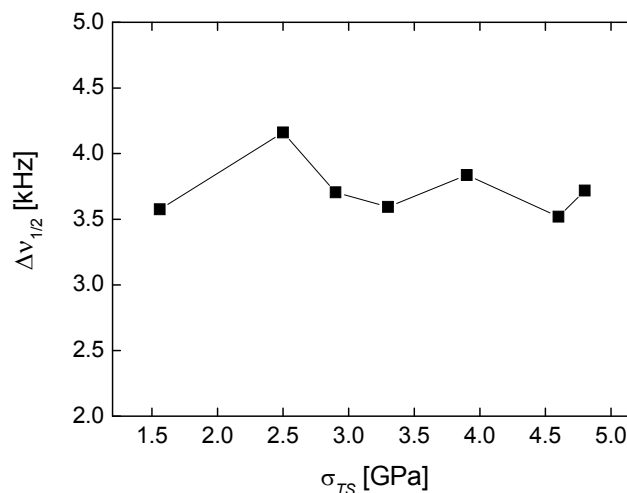


Fig. 5.15 The line-width of the 1H DAQ NMR spectra as a function of tensile strength for Dyneema[®] fibers.

5.3.2 Chain ordering and packing by van Vleck moments

From the fit of the initial part of the FID, in the range of 6.5 μs - 7.5 μs (Fig. 5.16), with a polynomial function of the following form:

$$G(t) = A_0 \cdot \left[1 - \frac{M_2 t^2}{2!} + \frac{M_4 t^4}{4!} - \frac{M_6 t^6}{6!} \right] \quad (5.9)$$

the second (M_2) and the fourth (M_4) van Vleck moments can be evaluated. These types of measurements have to be performed with NMR spectrometers at very high frequency where the dead time for the NMR probe is reduced to a few microseconds. This is the case with the 500 MHz Bruker NMR spectrometer used for this study, where the dead time is 6.5 μs (a typical FID recorded for Dyneema[®] fibers is shown in Fig. 5.14a).

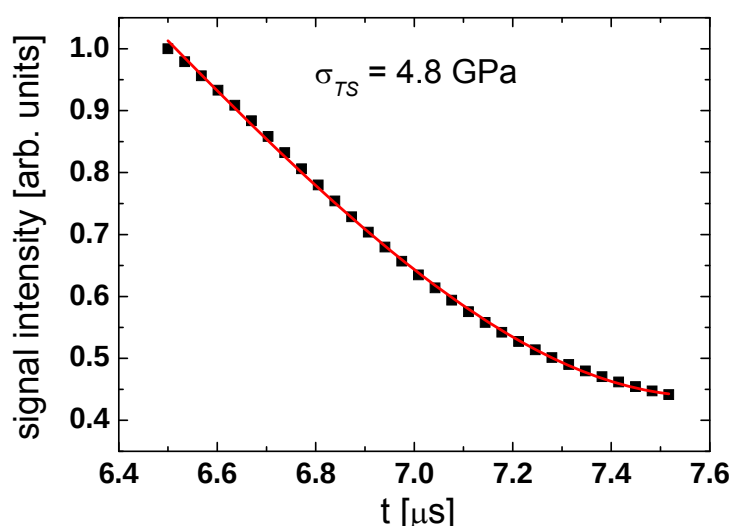


Fig. 5.16 The fit of the initial part of the FID recorded for the Dyneema[®] fiber with $\sigma_{TS} = 4.8$ GPa, using the polynomial function given in Eq. 5.9. The fit has been done only in the 6.5 μs – 7.5 μs range, taking into account the 6.5 μs dead time of the spectrometer.

The van Vleck moments of the dipolar broadened NMR spectrum are quantities related to the structure of the polymer. The interchain distances are expected to change upon drawing. Therefore this packing effect will modify the van Vleck moments. These changes in M_2 and M_4 for Dyneema[®] fibers as a function of tensile strength are shown in Fig. 5.17a,b. Both M_2 and M_4 increase about three times with σ_{TS} . That will correspond to an increase in the polymer chain packing and mass density. The ratio M_4/M_2^2 is a quantity that describes the “rigidity” of the structure in the presence of chain motions. For an ideal rigid structure this ratio is $M_4/M_2^2 = 3$. Figure 5.17c shows that the crystalline domains in mechanically drawn Dyneema[®] fibers

with $\sigma_{TS} \geq 2.5$ GPa have a packed structure with reduced chain motions, as the M_4/M_2^2 values are quite close to that of an ideal rigid.

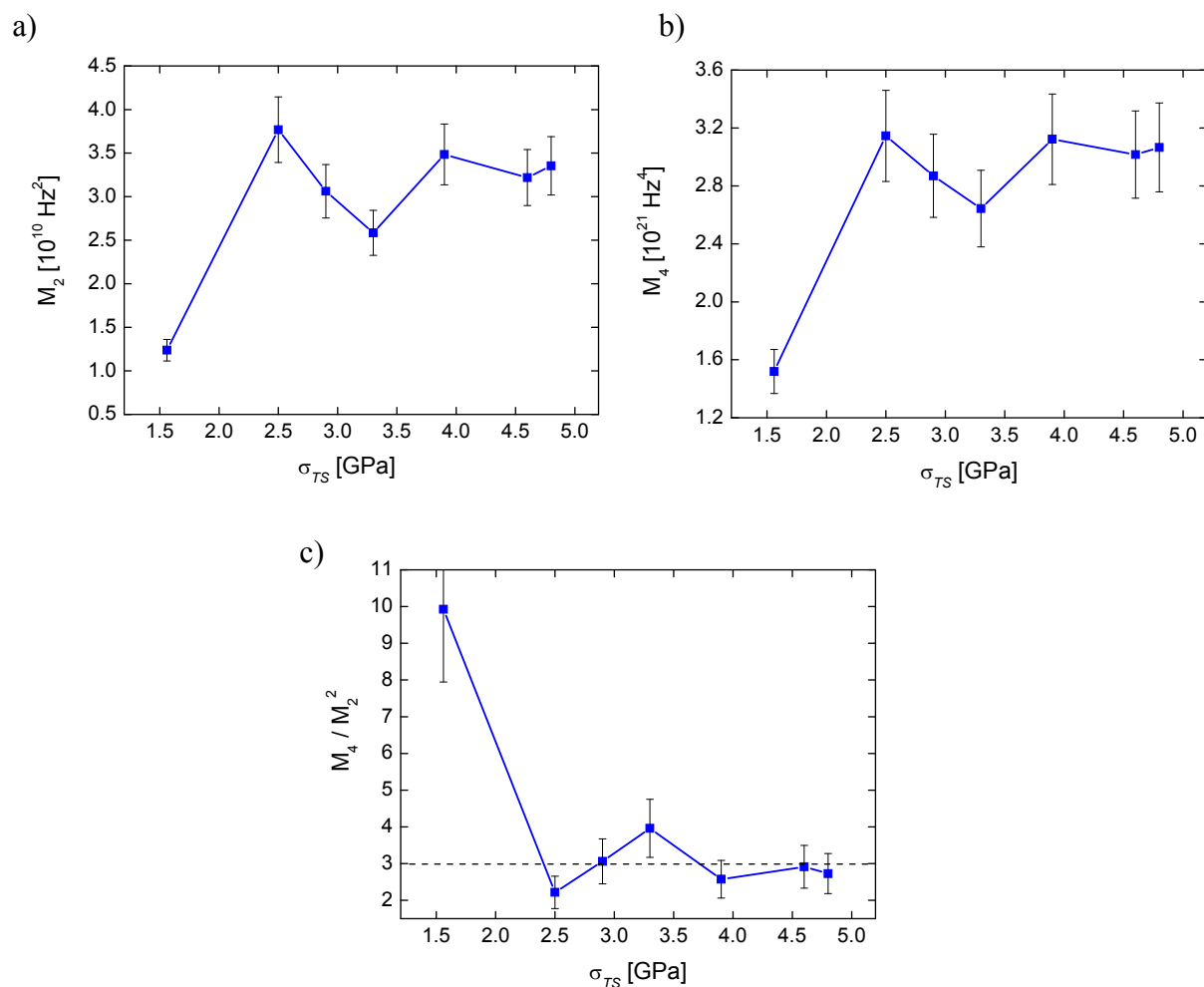


Fig. 5.17 a) M_2 and b) M_4 van Vleck moments and c) the ratio M_4/M_2^2 for UHMWPE Dyneema[®] fibers as a function of tensile strength σ_{TS} .

5.3.3 Domain sizes of drawn Dyneema[®] fibers by ¹H spin-diffusion NMR

Quantitative determination of the domain sizes is a difficult task for many physical methods including spin-diffusion NMR. In this latter case the difficulties are mainly related to: (i) the accurate evaluation of the spin diffusivities (D) and (ii) to the knowledge of the morphology. Nevertheless, the NMR spin-diffusion method allows the estimation of the sizes of interface and mobile phase in macroscopically non-oriented and amorphous samples. Moreover, the trend in the changes of domain sizes as a function of tensile strength can be also investigated.

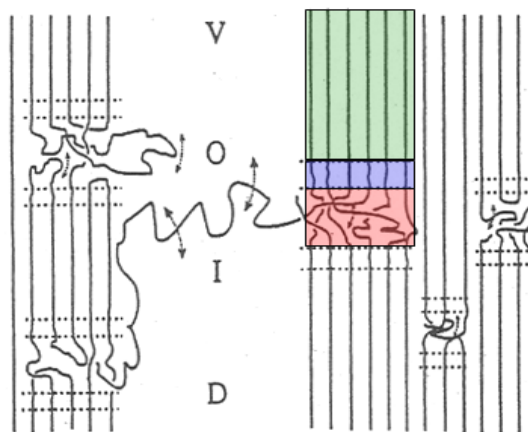


Fig. 5.18 Schematic representation of the morphology of a drawn PE fiber. One can distinguish a component with a high degree of chain ordering, corresponding to the rigid crystalline phase (green colored region), a less ordered component corresponding to the interface (blue colored region) and a disordered component corresponding to the mobile amorphous part (red colored region). The highly mobile chains are localized in the voids of the polymer.

Assuming a morphology of the drawn Dyneema[®] fiber similar to that described in the Fig. 5.18, ¹H spin-diffusion experiments were performed on the entire series of samples. However, based on the results obtained from the ¹H NMR wideline spectra decomposition, only two phases (rigid and mobile) have been considered for the samples with $\sigma_{TS} > 2.5$ GPa.

A double-quantum (DQ) dipolar filter has been used for the spin-diffusion measurements. This DQ filter, whose pulse sequence is shown in Fig. 2.1, initially selects only the magnetization from the rigid domain. Then, due to the spin-diffusion, the mobile phase gradually builds up as a narrow, easy detectable signal on top of the broad, originally selected NMR spectrum. The two different phases are better differentiated, increasing in this way the accuracy of the experimental data.

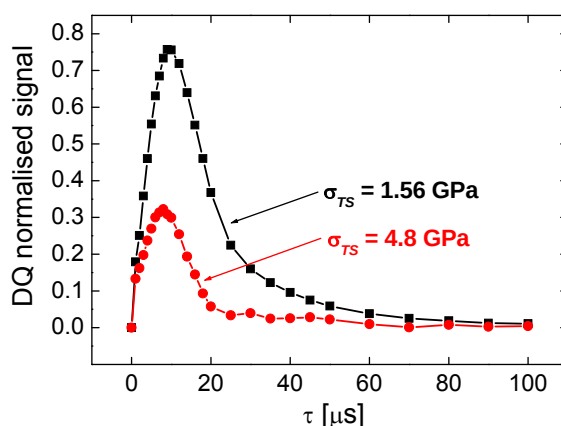


Fig. 5.19 Proton DQ build-up curves measured for Dyneema[®] fibers with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa. The NMR parameters are: $t_{DQ} = 5$ μ s and $\tau = 5$ μ s. As σ_{TS} increases, the maximum of the DQ build-up curves is shifted to smaller τ values, indicating an increase of the dipolar couplings in the more drawn fibers.

The efficiency of the DQ filter on Dyneema® fibers was tested in Fig. 5.19. It is evident that the maxima of the build-up curves arise for excitation/reconversion times τ of about 10 μs that correspond to the rigid region. The increase in the chain packing as the fibers are more and more drawn leads to a maximum that occurs at shorter τ values for the fiber with $\sigma_{TS} = 4.8$ GPa as compared to that with $\sigma_{TS} = 1.56$ GPa. DQ dipolar filter can be tuned in such a way that either the rigid or mobile domains are filtered. This feature is shown in Fig. 5.20. The split spectrum in Fig. 5.20a corresponds to the CH_2 groups that have the strongest dipolar couplings and for which the DQ coherences are excited with the highest probability at short τ values. For longer τ values the DQ filter acts like a Goldman-Shen dipolar filter, exciting only the magnetization from the mobile fraction (Fig 5.20b).

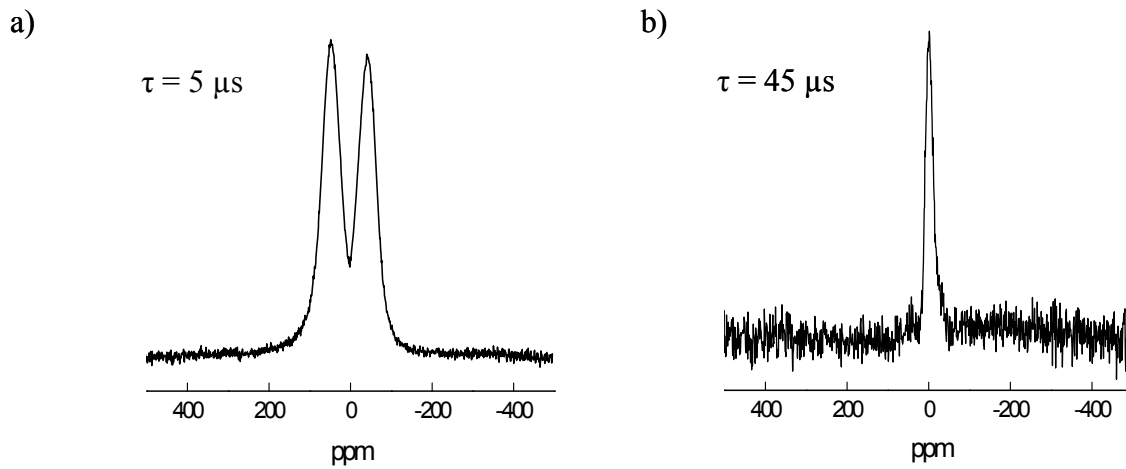


Fig. 5.20 Proton DQ edited spectra for Dyneema® fiber with the $\sigma_{TS} = 4.8$ GPa, using different filter times: a) 5 μs and b) 45 μs .

As mentioned before, ^1H spin-diffusion spectra were deconvoluted only into two spectral components: rigid and mobile. This is an acceptable approximation due to the small concentration of interface and highly mobile fraction. Moreover, at this stage the line shapes are considered Gaussian. These approximations will not essentially affect the trend of the domain sizes as a function of tensile strength σ_{TS} .

The spin-diffusivities were evaluated using the relationships:

$$D_{R,M} = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta\nu_{1/2} \quad (5.10)$$

where $\Delta\nu_{1/2}$ is the full linewidth at half-height and $\langle r^2 \rangle$ is the mean square distance between the nearest spins. For calculating $\langle r^2 \rangle$ the Discover program (version 2004.1) was used. The estimated weighted mean square distance $\langle r^2 \rangle$ equals approximately 0.0484 nm^2 . The spin-diffusion coefficients for rigid and mobile domains are shown in Table 5.3.

Table 5.3 Proton spin diffusivities for rigid (D_R) and mobile (D_M) fractions of Dyneema[®] fibers, as well as domain sizes d_R and d_M as a function of σ_{TS} . The errors are of the order of 10%.

σ_{TS} [GPa]	D_R [nm ² /ms]	D_M [nm ² /ms]	d_R [nm]	d_M [nm]
1.56	0.43	0.035	60	1.3
2.5	0.47	0.033	44	1.7
2.9	0.49	0.015	210	1.7
3.3	0.50	0.011	240	1.4
3.9	0.51	0.012	254	1.5
4.6	0.52	0.010	250	0.8
4.8	0.52	0.012	254	2

We assume that the spin-diffusion takes place in a heterogeneous polymer from a source R with low segmental mobility into a finite sink M with larger segmental mobility. The presence of an interface is neglected in the following considerations. The relationships describing the time evolution of the integral intensities of the NMR signals $I_R(t)$ and $I_M(t)$ for a spin-diffusion process of dimensionality n ($n = 1, 2$, and 3) can be obtained from reference Dem1. The spin magnetization in the source region (R) for an n -dimensional spin-diffusion process is given by

$$I_R(t) \approx \rho_R \left[2 \int_0^{d_R/2} m_R(x, t) dx \right]^n \quad (5.11)$$

where ρ_R is the number density of spins of the source R of size d_R and $m_R(x, t)$ is the space and time dependent concentration of the z spin magnetization. For a dipolar filter that selects only the magnetization of the R region, the spin magnetization in the sink region can be written as

$$I_M(t) = I_R(0) - I_R(t) \quad (5.12)$$

The quantity $m_R(x, t)$ is given by

$$m_R(x, t) = \frac{\rho_R d_R m_{0R}}{\rho_R d_R + \rho_M d_M} - \sum_{m=1}^{\infty} 2m_{0R} \sin[kd_M \beta_m] \cos[x\beta_m] \exp[-D_R \beta_m^2 t] \beta_m^{-1} \cdot \{ [\sigma d_R + kd_M] \cos[d_R \beta_m] \cos[kd_M \beta_m] - [\sigma kd_M + d_R] \sin[d_R \beta_m] \sin[kd_M \beta_m] \}^{-1} \quad (5.13)$$

where d_M is the size of the sink, ρ_M is the number density of spins in the region M, $k = (D_R / D_M)^{1/2}$, and $\sigma = k\rho_R / \rho_M$. The spin-diffusion coefficients in the regions R and M are denoted by D_R and D_M respectively. The quantities β_m ($m=1,2,3,\dots$) are the roots of a trigonometric equation defined in the reference [Wan1].

Proton spin-diffusion data are shown in Fig. 5.21a,b for the samples with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa, respectively.

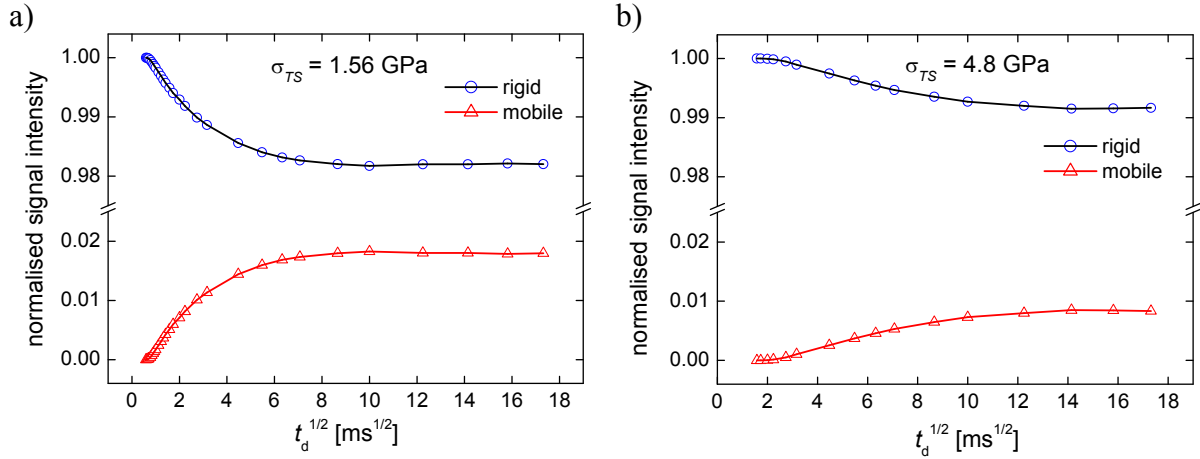


Fig. 5.21 Normalized signal intensity from ^1H spin-diffusion experiment for Dyneema[®] fibers with tensile strength a) $\sigma_{TS} = 1.56$ GPa and b) $\sigma_{TS} = 4.8$ GPa.

The domain sizes can be evaluated from the spin-diffusion decay and buildup curves of Fig. 5.21 using the simple one-dimensional (1D) morphology of PE. It is clear that this is an approximation for the two-dimensional (2D) morphology shown in Fig. 5.18. The spin-diffusion data reveal that in the approximation of two components the magnetization flows from the rigid phase to a highly mobile phase with the concentration of 1 – 2 %. Therefore, the measured domain sizes have to be considered not along the PE fibrils but in the transverse direction, i.e. in the direction of the voids or in the region between crystallites where loose chains are localized.

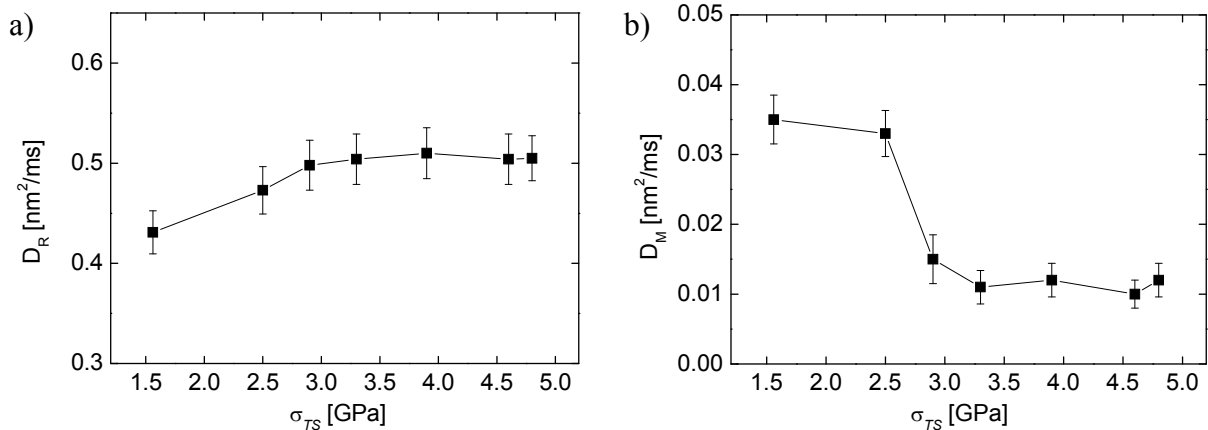


Fig. 5.22 The dependence of a) rigid and b) mobile spin-diffusivities on tensile strength σ_{TS} .

The data were fit with the solutions of the spin-diffusion equation for 1D case ($n = 1$) (see Eq. 5.11). The continuous lines in Fig. 5.21 show these fits. The spin-diffusivities used for these fits are given in Table 5.3 and shown in Fig. 5.22. As expected D_R increases with σ_{TS} due to the chain packing in the rigid domains. The spin diffusivity D_M becomes smaller due to increased disorder induced in the mobile chains by the drawing process.

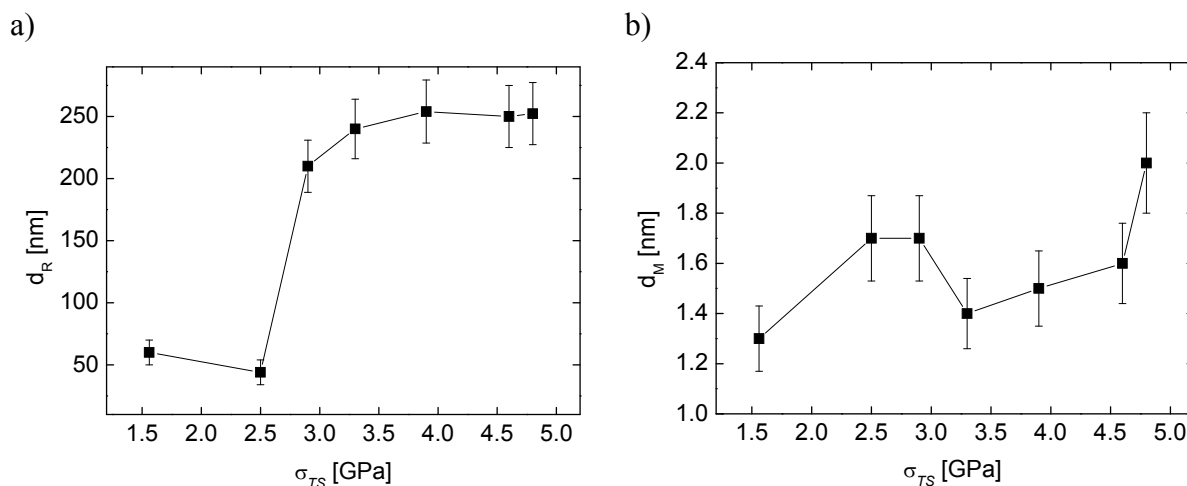


Fig. 5.23 a) Rigid and b) mobile domain sizes as a function of tensile strength for Dyneema® fibers.

The dependence of the domain sizes d_R and d_M on σ_{TS} for Dyneema® fibers is presented in Fig. 5.23. The value of the rigid domain for $\sigma_{TS} = 1.56$ GPa is about 60 nm. The drawn Dyneema® fiber with $\sigma_{TS} = 2.5$ GPa shows the same behaviour like that reported above for the phase composition and chain dynamics. That could be related to the different temperature used during the drawing process for $\sigma_{TS} = 2.5$ GPa. The rigid domain size increases about four times for samples with $\sigma_{TS} \geq 2.9$ GPa, in agreement with the crystallinity. The mobile domain sizes are small, of the order of few nm. Again the Dyneema® fiber with $\sigma_{TS} = 2.5$ GPa differs from the general trend. A small increase in the mobile domain size is evident for the larger values of σ_{TS} . This could be related to the increase in the number of voids for highly drawn UHMWPE fibers.

5.3.4 Chain orientation by ^1H solid-state NMR

Mechanical deformation typically induced by drawing, compression or rolling, can lead to anisotropy at the macroscopic level where, in effect, the orientation dependence that characterizes the structural units at the molecular level is retrieved in part in the bulk: ultra-high-modulus fibers are notable examples.

In materials as morphologically complex as polymers, one is inevitably concerned with macroscopically averages, or moments, of the distribution of structural units. A practical consequence of the NMR based on the tensorial properties of dipolar couplings is the distribution of moments derived in such experiments, that can be used directly to model different other tensorial properties like mechanical moduli [McB1].

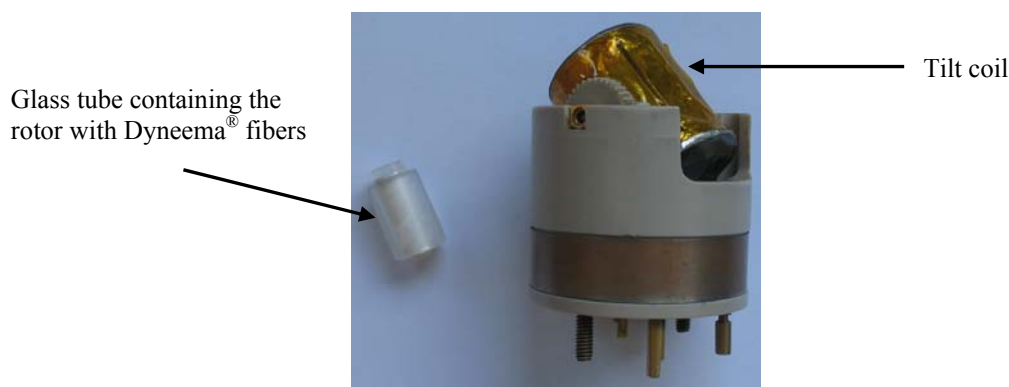


Fig. 5.24 NMR radio-frequency tilt coil (right). The zirconium oxide rotor filled with Dyneema® fibers is inserted into a glass tube and afterwards, together with it, into the tilt coil.

The measurements of the oriented drawn Dyneema® fibers by ^1H wide-line NMR spectroscopy were done with a solid-state Bruker NMR spectrometer operating at the proton frequency of 200 MHz, using a special “tilt” coil, which can be rotated at different angles with respect to the $\mathbf{B}_0$ magnetic field. This coil is shown in Fig. 5.24. The fibers were packed together in the rotor, aligned by hand, in the best possible way, with the rotor axis.

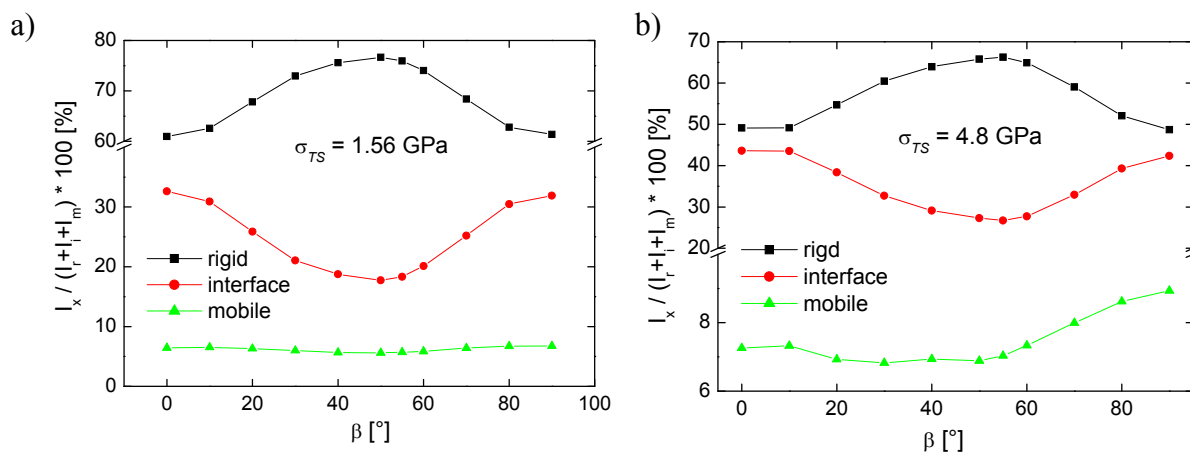


Fig. 5.25 Orientation dependence of the relative intensities of the ^1H spectral components for Dyneema® fiber with a) $\sigma_{TS} = 1.56 \text{ GPa}$ and b) $\sigma_{TS} = 4.8 \text{ GPa}$.

The first quantity measured was the integral intensity of the ^1H NMR spectral components, obtained by spectral deconvolution, as a function of the β angle between the direction of the rotor axis and the direction of the static magnetic field (Fig. 5.25). Only the Dyneema® fibers

with the tensile strength $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa were considered for these measurements.

In oriented PE fibers there is a dominant influence of the methylene internuclear vectors on the angular dependence of the second van Vleck moment M_2 and associated spectral linewidth, due to the short-range nature of the dipolar interaction (Fig. 5. 26). The angular dependences of the $I_x(\beta)$ quantities can be then explained by the following arguments. The transverse magnetization relaxation time $\frac{1}{T_2}$ is related to the second van Vleck moment M_2

by the relationship

$$\frac{1}{T_2} \propto (M_2)^{1/2} \quad (5.14)$$

i.e.:

$$T_2 \propto (M_2)^{-1/2} \quad (5.15)$$

Based on the above equations, the length of free induction decay (FID) depends on the orientation angle. From Fig. 5.26 it is evident that for the crystalline phase the quantity $(M_2(\beta))^{-1/2}$ has a maximum, i.e. the $T_2(\beta)$ goes also through a maximum, where the FID has the longest time evolution.

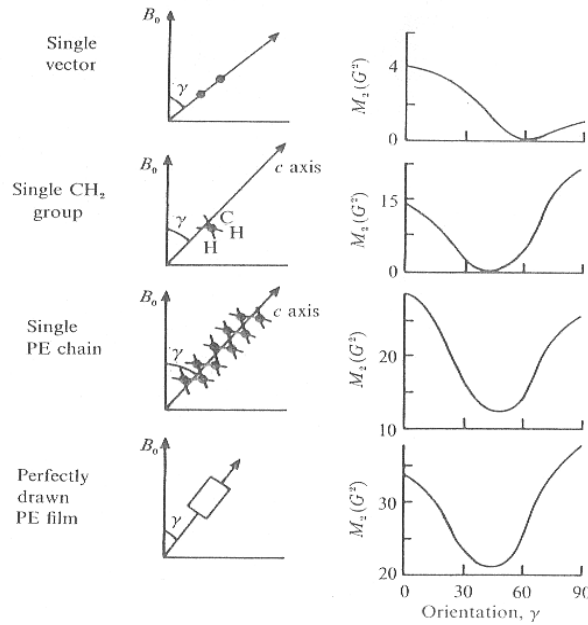


Fig. 5.26 Diagram illustrating the development of anisotropy in M_2 for a highly uniaxially oriented sample of crystalline PE.

The dead time of the rf coil at 200 MHz spectrometer is about $7.5 \mu\text{s}$ and cuts the fast FID of all the UHMWPE phases. The highest amount of crystalline phase is edited at the

magic angle. A maximum of $I_{rigid}(\beta)$ is detected at $\beta_m = 54.7^\circ$ as it is evident from the Fig. 5.25. The polymer chains at the interface show also an angular dependence but in the opposite direction. This can be explained by a different orientation of the polymer chains and of the internuclear vector of their methylene groups. The distribution of the orientations for both cases is relatively large and dominated by the imperfection in the alignment of the fibers. The highly mobile fraction is mainly non-oriented for $\sigma_{TS} = 1.56$ GPa. Nevertheless, a small orientation is present for the mobile PE chains for $\sigma_{TS} = 4.8$ GPa (Fig. 5.25).

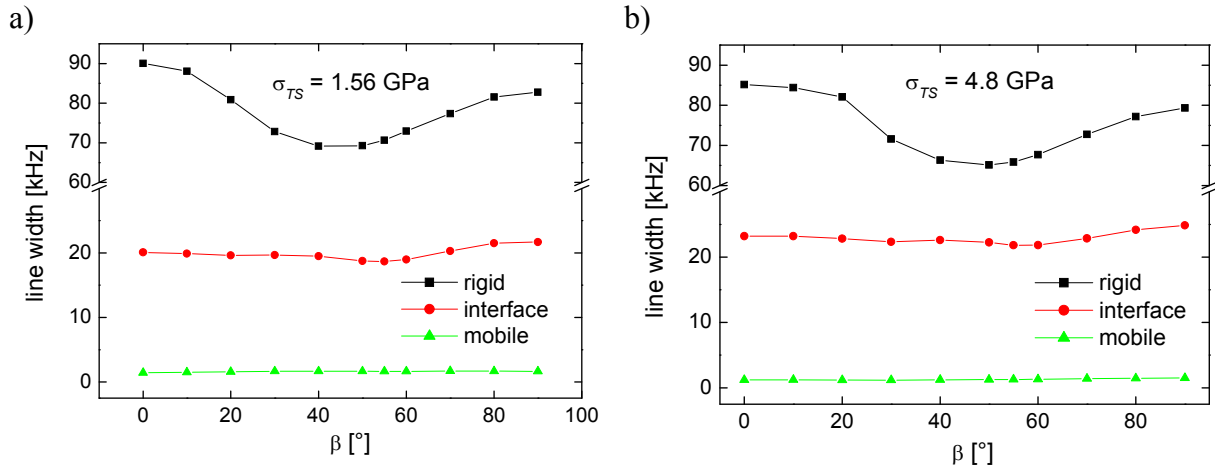


Fig. 5.27 Orientation dependence of the $\Delta v_{1/2}$ for the ^1H spectral components of Dyneema[®] fiber with a) $\sigma_{TS} = 1.56$ GPa and b) $\sigma_{TS} = 4.8$ GPa.

The second van Vleck moment, which is orientation dependent, can be directly measured from the NMR spectra linewidth at the half-height $\Delta v_{1/2}$ (Fig. 5. 27). The following relationship is valid

$$\Delta v_{1/2} \propto (M_2)^{1/2} \quad (5.16)$$

In the same time we have to point out that the value $\Delta v_{1/2}$ is also affected by the dead time filtering (DTF). That is expected to be a small effect for the case of the interface and the mobile components. These dependences are shown in Fig. 5.27 for the samples with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa, and are similar to those shown for a model oriented polymer fiber in Fig. 5.26.

5.3.5 CP-MAS ^{13}C NMR spectra

Using the standard cross-polarization NMR technique under MAS, the ^{13}C spectra for all the samples in our series were recorded. The spectra were decomposed into 4 components, using a numerical procedure of deconvolution [Mas1] (Fig. 5.28).

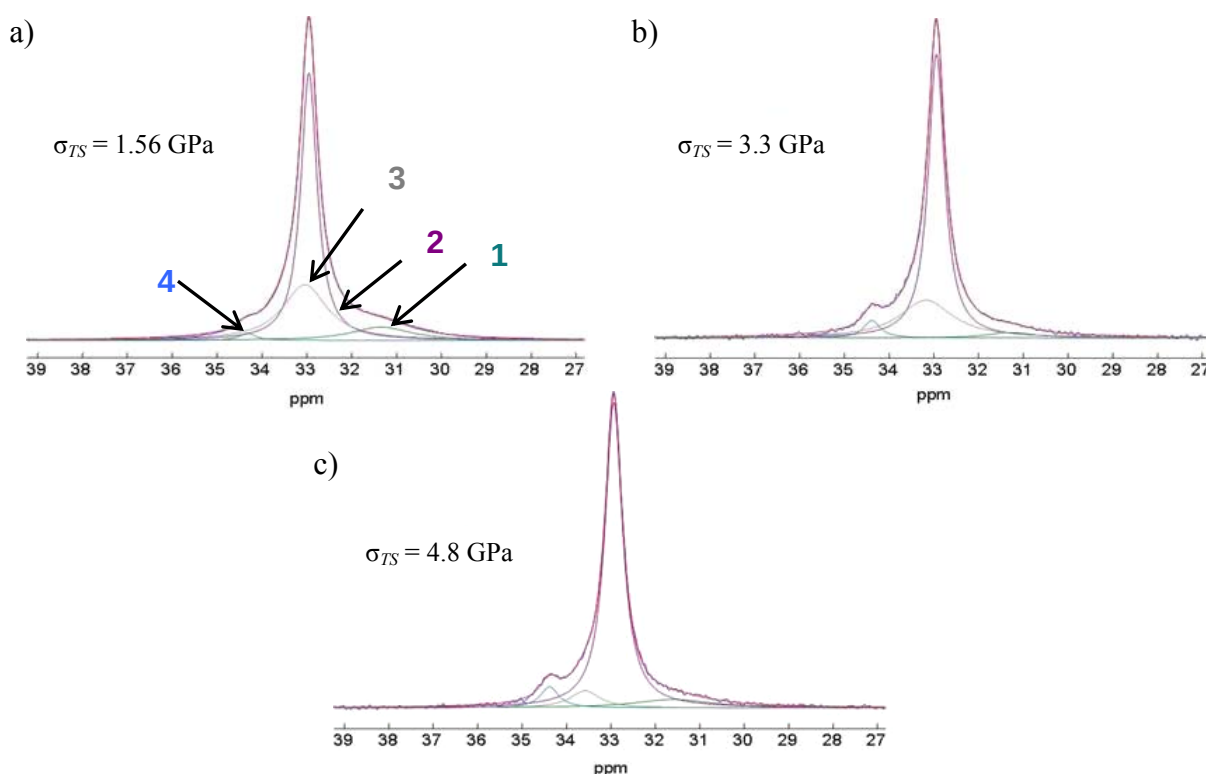


Fig. 5.28 ^{13}C NMR spectra of Dyneema[®] samples with tensile strength a) $\sigma_{TS} = 1.56$ GPa b) $\sigma_{TS} = 3.3$ GPa and c) $\sigma_{TS} = 4.8$ GPa. The numerical decomposition of the spectra with the "dmfit program" [Mas1] was based on a 4-component model: **1**, a large band around 29-33 ppm corresponding to the gauche containing amorphous phase; **2**, the 32.8 ppm peak of the orthorhombic signals; **3**, all-trans intermediate-component signal around 33 ppm; and **4**, the monoclinic crystalline resonance at ~ 34.5 ppm.

In the ^{13}C CP-MAS spectra additional intensity appears downfield of the sharp resonance at 32.8 ppm identified with the orthorhombic crystals [Ear1]. These signals are due to all-trans chains, but with molecular packing different from that of the orthorhombic crystalline lattice [Van1]. It is not known however if this fraction is exclusively or only partially interfacial. One believes that it possibly contains contributions from several distinct morphological components, such as interfacial segments, isolated tie molecules, tie-molecule bundles, and even small disordered crystallites. Looking at the complete series of spectra from $\sigma_{TS} = 1.56$ GPa to $\sigma_{TS} = 4.8$ GPa, an important alteration of the intensity of this intermediate-component signal as a function of σ_{TS} can be observed. In the same time the position of the line is shifted downfield with increasing σ_{TS} .

In the spectral region of the gauche-containing amorphous phase, around 29-33 ppm [Ear1], indications of line-shape changes due to drawing are also observed. The overall intensity of the amorphous signals decreases relative to the crystalline peak, and a slight downfield shift is detectable with increasing σ_{TS} .

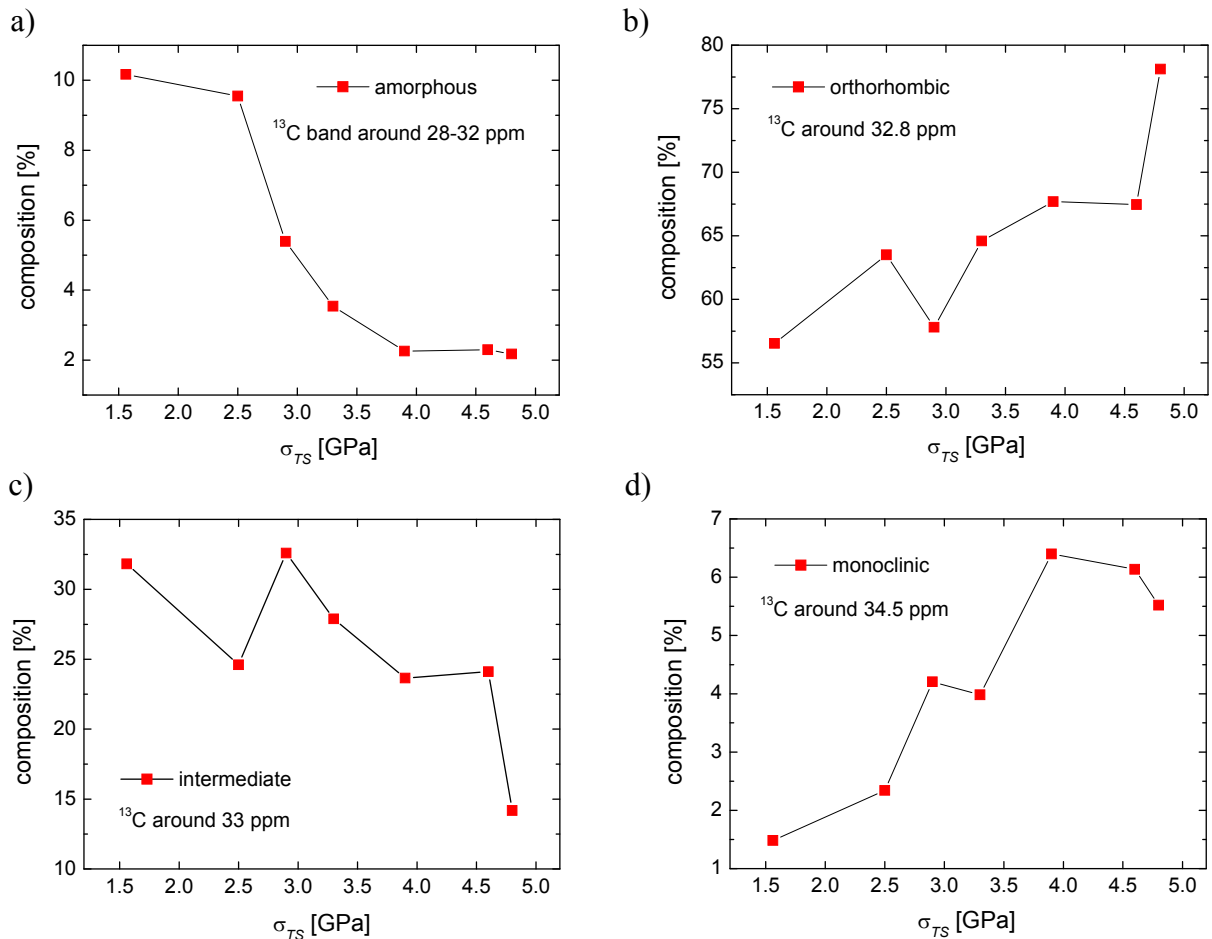


Fig. 5.29 The relative fractions of drawn Dyneema® fibers in terms of the a) amorphous, b) orthorhombic, c) intermediate and d) monoclinic fractions plotted against tensile strength σ_{TS} .

Clearly, the uniaxial mechanical drawing leads to structural changes that are reflected in the spectra. Using the decomposition of the ^{13}C spectra, the percentage of each of the morphological components has been calculated as a function of tensile strength. The dependence of the relative composition on σ_{TS} is shown in Fig. 5.29. The amorphous phase starts to decrease with increasing σ_{TS} , from about 10% for $\sigma_{TS} = 1.56$ GPa to almost 2% for $\sigma_{TS} = 4.8$ GPa, whereas the orthorhombic and monoclinic crystalline parts increase as the fibers are more and more drawn. An important increase of about 22% is detected for the orthorhombic component, showing us that the Dyneema® fibers become more and more crystalline with increasing σ_{TS} . A dramatic decrease from about 32% to about 15% of the intermediate phase as a function of σ_{TS} can be seen from Fig. 5.29c.

The chain mobility of Dyneema® fibers has been investigated further on in terms of values of the peak's linewidth at half-height ($\Delta\nu_{1/2}$) in the ^{13}C NMR spectra (Fig. 5.30). One can observe an increase of the linewidths for the crystalline orthorhombic and monoclinic parts as a function of σ_{TS} (Fig. 5.30b,d), indicating an increase in the rigidity of these

morphological components as the samples are more and more drawn. The same phenomenon is characteristic for the intermediate component too (Fig. 5.30c). However, the higher values of the linewidth compared to that of the crystalline phase, indicates local disorder in conformation or, more likely, in chain packing for the intermediate component.

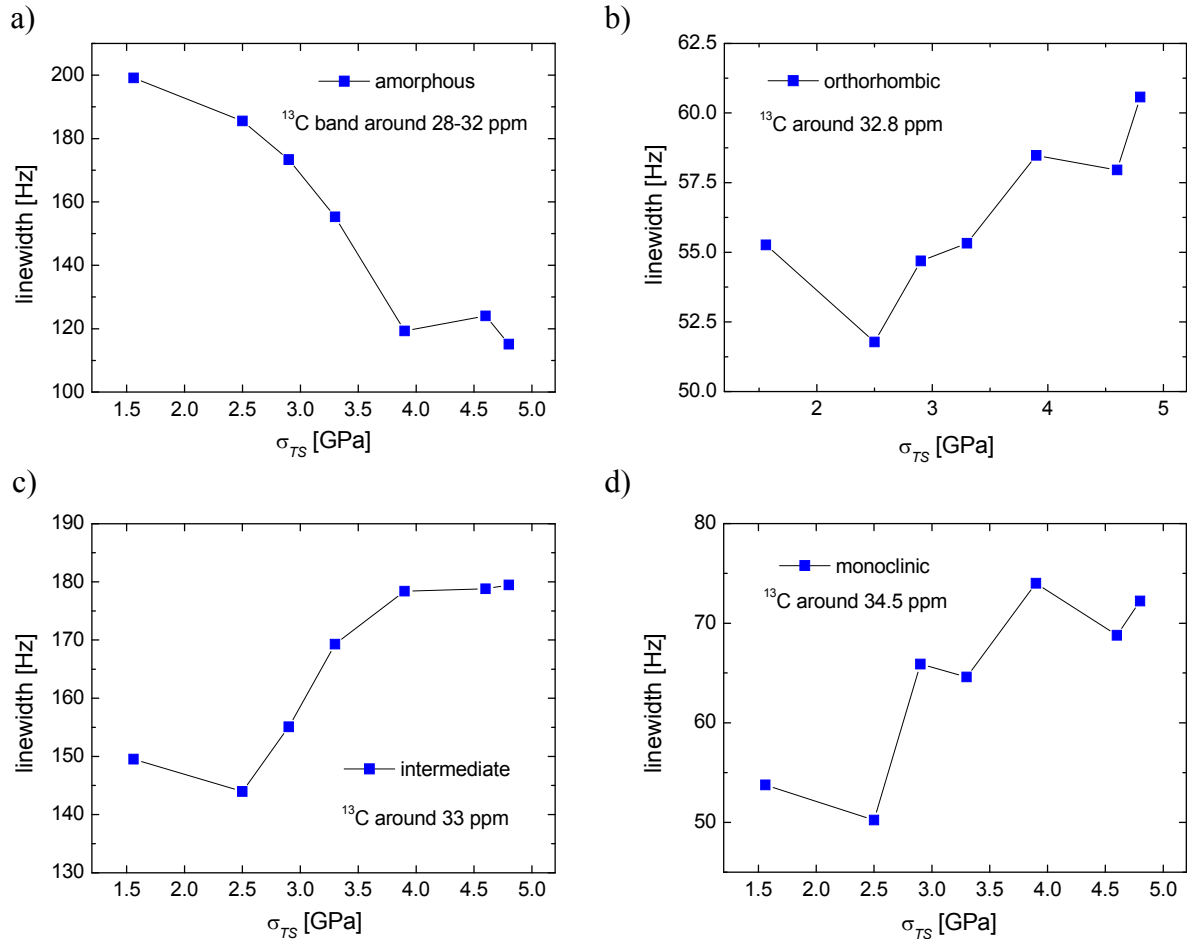


Fig. 5.30 The dependence of the a) amorphous, b) orthorhombic, c) intermediate and d) monoclinic fractions' linewidth at half-height against the tensile strength σ_{TS} , for drawn Dyneema® fibers.

A very interesting result has been obtained for the amorphous phase. Even if this morphological component decreases with increasing σ_{TS} , the decrease of the linewidth in Fig. 5.30a indicates an increase in mobility. So the Dyneema® fibers become more and more crystalline as σ_{TS} increases, with the crystalline phase showing a higher rigidity as going from from $\sigma_{TS} = 1.56$ GPa to $\sigma_{TS} = 4.8$ GPa, whereas, in the same time, the amorphous phase is less but more mobile. This conclusion is sustained by the results obtained by other NMR methods, as shown below.

5.3.6 Mobility characterization by ^{13}C - ^1H WISE NMR

The motional amplitude of CH_2 groups can be estimated from their ^1H line width. Using a sophisticated but very powerful technique which is the 2D wide-line-separation (WISE) spectroscopy, ^1H spectra of the various morphological components in the drawn UHMWPE microstructure can be obtained using ^{13}C as a spy nucleus.

Two examples of the WISE spectra for $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa samples are shown in Fig. 5.31a,b. Knowing the chemical shift of the different morphological components in the ^{13}C dimension, the ^1H slices corresponding to each of these have been extracted. The ^1H wide-line spectrum of the orthorhombic crystallites (Fig. 5.31d) at 32.8 ppm of ^{13}C is very broad, about 120 kHz full width at half-maximum, indicating a highly rigid component with very strong ^1H - ^1H dipolar couplings. Also, the crystalline spectrum reveals two maxima reminiscent of a Pake pattern, which can be attributed to the geminal ^1H - ^1H dipolar coupling.

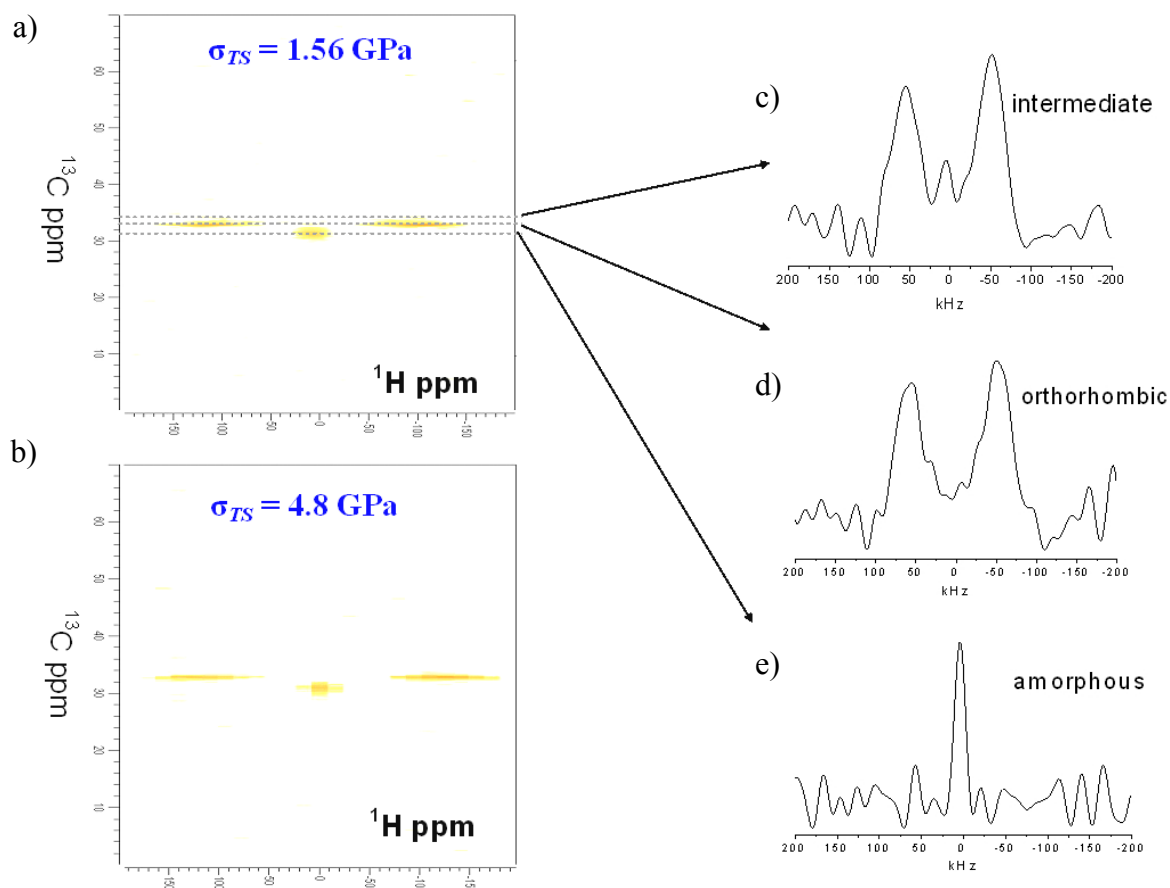


Fig. 5.31 The 2D WISE spectra for Dyneema[®] fibers with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa and the ^1H slices corresponding to the different morphological components in the structure of drawn UHMWPE.

The ^1H wide-line pattern of the intermediate-component (cross section Fig. 5.31c) at 33 ppm of ^{13}C has a slightly reduced half-width of about 110 kHz, denoting an increase in the

segmental mobility compared to that of the crystalline phase. The ^1H slice of the amorphous component (Fig. 5.31e) at 31 ppm shows a full width of half-maximum of about 12 kHz, indicative of high segmental mobility.

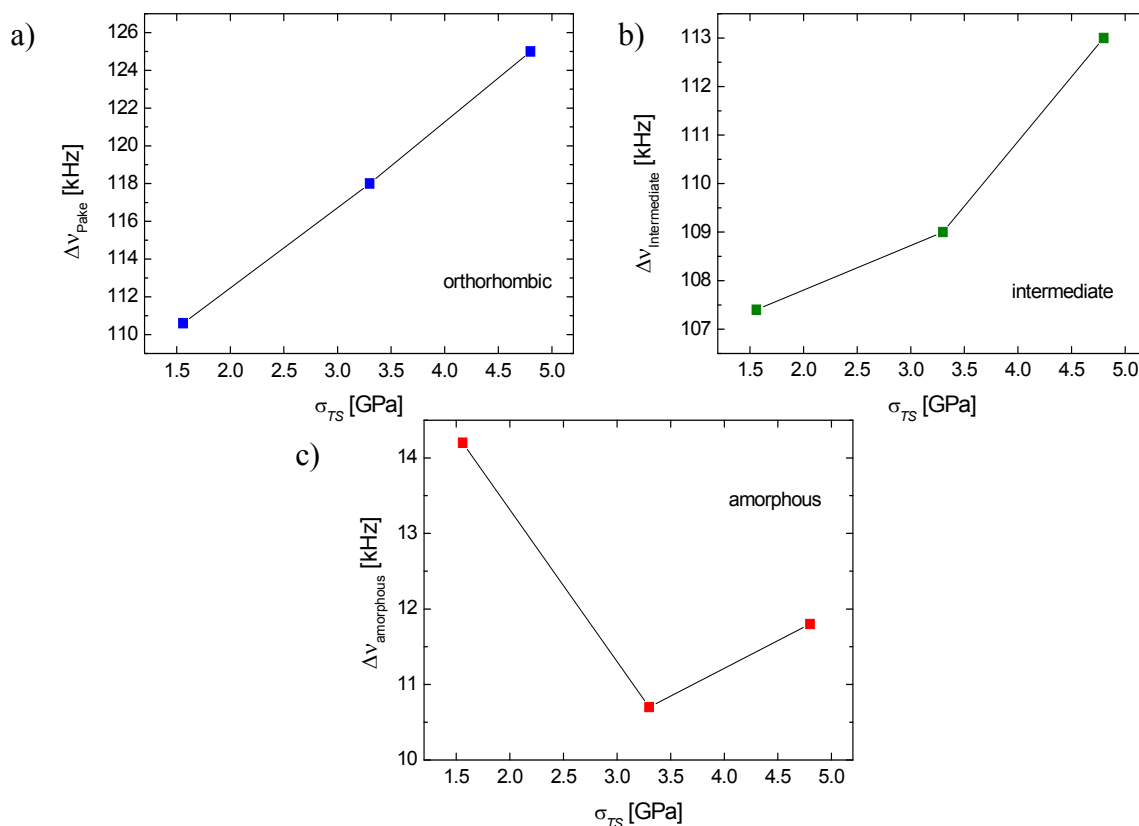


Fig. 5.32 The dependence on tensile strength of the linewidth $\Delta v_{1/2}$ taken from ^{13}C - ^1H WISE spectra for the a) orthorhombic, b) intermediate and c) amorphous phases.

The fraction-selective chain dynamics of Dyneema[®] fibers has been studied as a function of σ_{TS} , by looking at the values of the linewidth at half-height (Fig. 5.32). The increase in $\Delta v_{1/2}$ with σ_{TS} for the orthorhombic and intermediate components shows an increase in rigidity for these fractions as σ_{TS} increases, whereas, the same interesting result as before, the decrease in the linewidth values for the amorphous part indicates an increase in the mobility of this components as the fibers are more and more drawn.

5.3.7 ^{13}C $T_{1,\text{C}}$ filtered spectra of partially oriented Dyneema[®] fibres

Detailed and quantitative information about the polymer morphology can be derived from NMR spectra that are discriminating to specific components in the microstructure. Such selectivity can be achieved by utilizing differences in spin relaxation times, which are usually based on differences in the segmental mobility of the various components. In semicrystalline

polymers far above the glass transition of the amorphous domains, a particularly useful distinction is made according to the ^{13}C longitudinal ($T_{1,C}$) relaxation time.

Thus to characterize the intermediate components in the morphology of UHMWPE, NMR experiments are required that allow its selective observation based not only on its all-trans chemical shift of more than 32.8 ppm, but also in terms of its distinctive intermediate ^{13}C longitudinal (T_1) relaxation time. In earlier studies of various forms of polyethylene [Mow1 and references therein], the intermediate $T_{1,C}$ has generally been estimated to differ from the ^{13}C T_1 relaxation times of both the amorphous and crystalline components by at least an order of magnitude. Segments in the amorphous regions have a short $T_{1,C}$, less than one second, due to fast molecular mobility, while the $T_{1,C}$ of the crystallite core exceeds 100 s. For interfacial regions, intermediate $T_{1,C}$ values are found for a variety of reasons, which prominently include transferred relaxation due to chain diffusion from amorphous to crystalline regions in polyethylene [Sch1].

Selective relaxation experiments require suppression of both the crystalline and the amorphous signals, based on these differences in T_1 values. Most traditional experiments do not separate resonances of the crystalline and intermediate components, or of the intermediate and amorphous components. For instance, cross-polarization suppresses the signals of the highly mobile amorphous components, since they have reduced dipolar couplings and CP efficiencies, but retains both crystalline and intermediate resonances. Single-pulse excitation of ^{13}C can select the mobile components and could be combined with a ^{13}C T_1 filter to retain only the intermediate component(s). However, this procedure reduces the sensitivity greatly, due to the loss of CP enhancement and the necessity of long recycle delays (>5 s) to ensure sufficient relaxation of the magnetization within the intermediate component(s).

A series of ^{13}C CP/MAS spectra with varying $T_{1,C}$ filter time were acquired for the drawn Dyneema[®] fibers. As examples, the spectra recorded for $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa samples are shown in Fig. 5.33, having the fibers cut as in illustrated Fig. 5.1. Using the filter times $t_{za} = 1$ ms and $t_{zb} = 1$ s (see Fig. 5.3), and taking the difference between the ^{13}C spectra obtained for these filter times, we can isolate the signal coming only from the intermediate chain segments.

Spectra obtained as the difference between $t_{za} = 1$ ms and $t_{zb} = 1$ s $T_{1,C}$ filtered signals are presented for $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa samples in Fig. 5.34, parts a and b respectively. It can be seen that the intermediate component for Dyneema[®] fibre with $\sigma_{TS} = 4.8$ GPa is more oriented compared to that of the fiber with $\sigma_{TS} = 1.56$ GPa sample, as an increase of the chemical shift anisotropy can be observed.

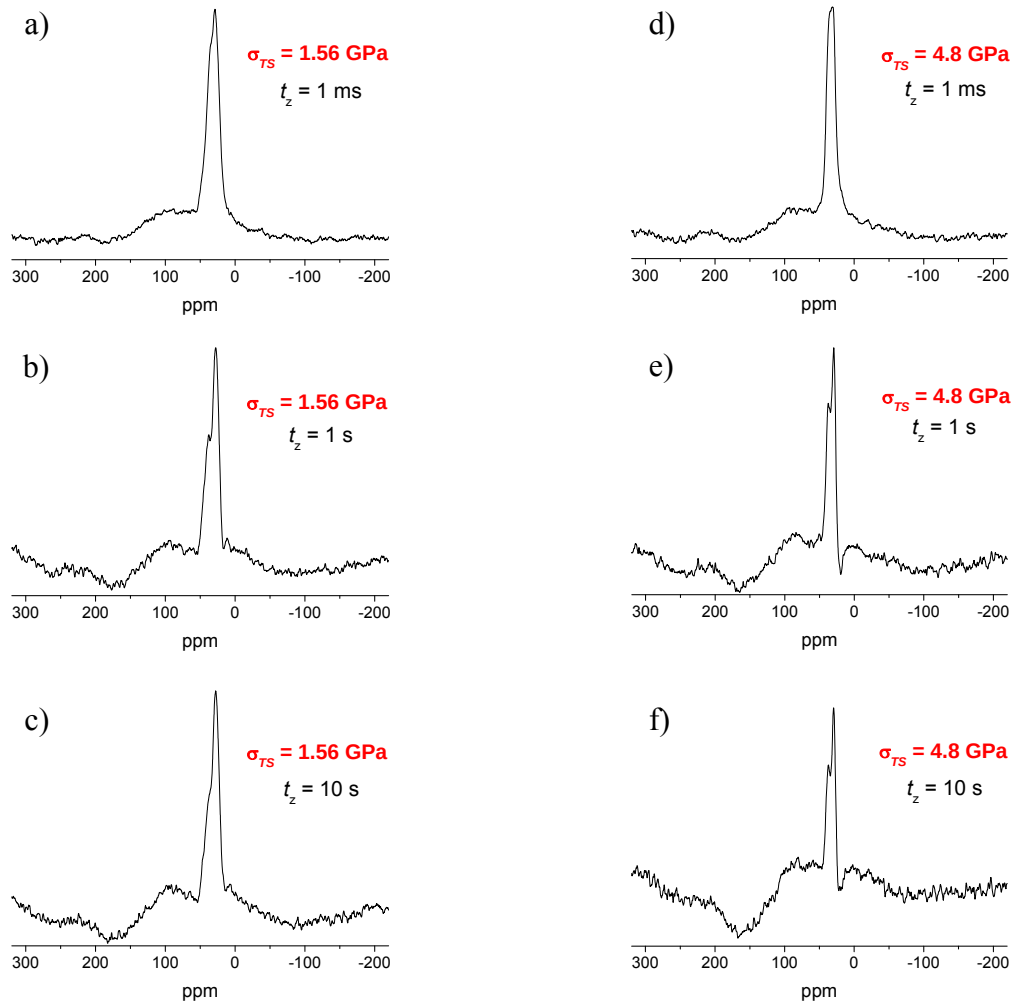


Fig. 5.33 ^{13}C T_{1C} filtered NMR spectra for different t_z filter times for Dyneema[®] fibers with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 4.8$ GPa at magic angle orientation. a), d) Choosing $t_z = 1$ ms, the signal coming only from the component with the shortest T_{1C} longitudinal relaxation time, i.e. the amorphous component it has been recorded. b), e) For longer filter times ($t_z = 1$ s), the signal recorded is made by the contributions of both amorphous and intermediate phases. c), f) Choosing even longer filter times ($t_z = 10$ s), a part of the magnetization of crystalline component (the component with the longest T_{1C} longitudinal relaxation time) recovers, so that the final spectrum includes the contributions of the amorphous phase, intermediate phase but also of a part of the crystalline phase.

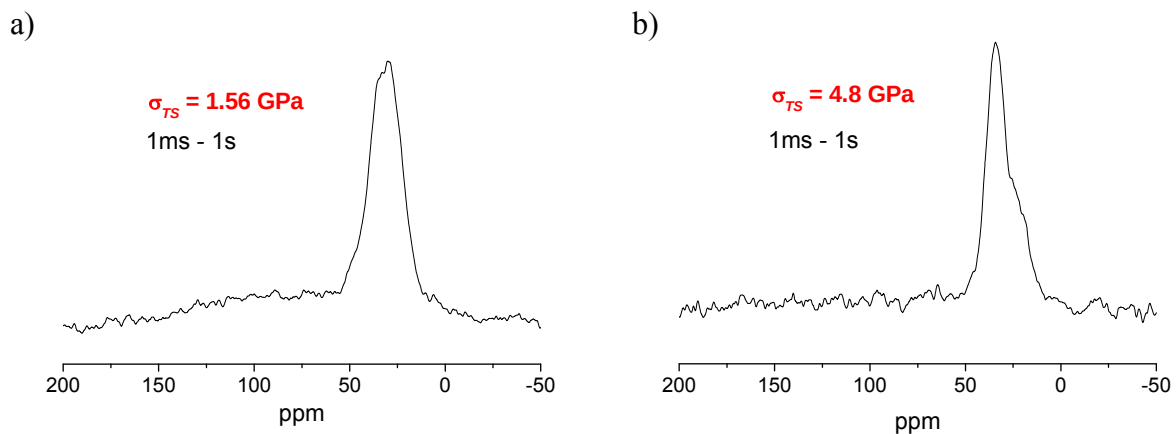


Fig. 5.34 ^{13}C T_{1C} filtered NMR difference-spectra for a) $\sigma_{TS} = 1.56$ GPa and b) $\sigma_{TS} = 4.8$ GPa samples.

The relatively large line widths indicate significant disorder relative to the crystalline part. Looking at the dependence of the linewidth at half-height on tensile strength (Fig. 5.35a), the decrease of the values from about 20 ppm to about 16.5 ppm going from $\sigma_{TS} = 1.56$ GPa to $\sigma_{TS} = 4.8$ GPa samples indicates that the local disorder in chain conformation for the intermediate component decreases with tensile strength.

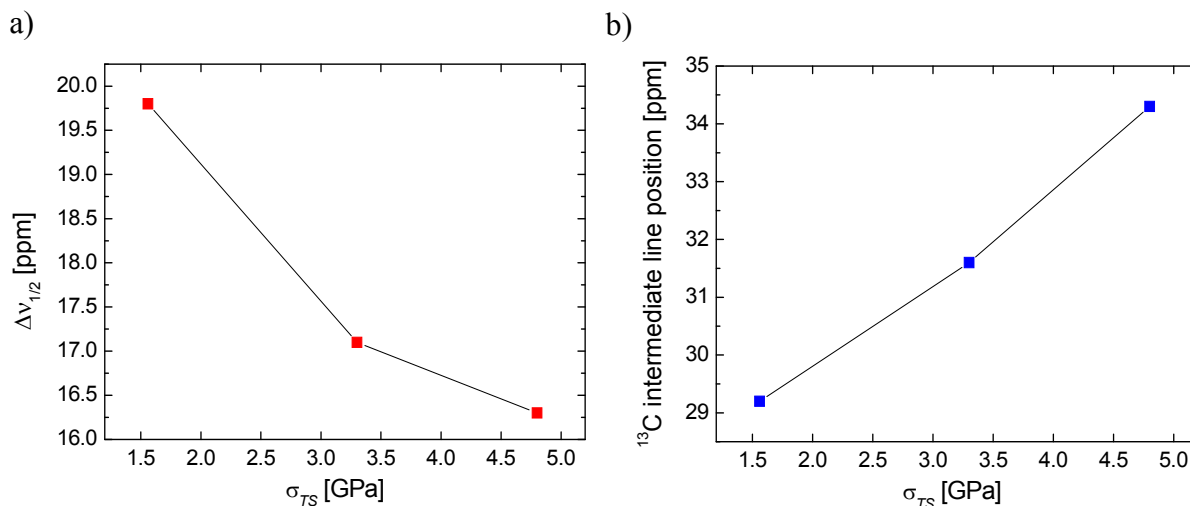


Fig. 5.35 The dependence on σ_{TS} of a) intermediate fraction's linewidth and b) intermediate fraction's line position for ^{13}C $T_{1\rho}$ filtered spectra.

The chemical shift range (~ 30 – 34.4 ppm, Fig. 5.35b) of the intermediate component shows that these chain segments have primarily all-trans conformations. The observed increase in the chemical shift of ^{13}C with σ_{TS} proves more denser chain packing in the intermediate fraction [Van1].

5.3.8 Mobility Characterization by ^{13}C Chemical Shift Anisotropy

A quantitative determination of the motional amplitude from WISE line shapes is challenging, due to the multispin character of the ^1H - ^1H dipolar interactions. The effects of fast motions on the chemical shift anisotropy of the $^{13}\text{CH}_2$ groups are more amenable to a quantitative evaluation of the motional amplitude. The chemical shift anisotropy in UHMWPE can be analyzed most easily with experiments without sample rotation, i.e., static NMR. For this second set of measurements in which the ^{13}C $T_{1\rho}$ filter has been used, in order to eliminate the effects of sample orientation on the spectral line shape, a macroscopically isotropic powder-like sample was prepared as shown in Fig 5.2. This induces no additional artifacts in our measurements, as the artificially increased presence of stress-induced microstructures would not interfere much with probing local segment dynamics.

Applying the ^{13}C $T_{1\rho}$ filter, the spectra corresponding to different filter times ($t_z = 1$ ms and $t_z = 1$ s) were recorded for the entire series of Dyneema[®] samples going from $\sigma_{TS} = 1.56$ GPa to $\sigma_{TS} = 4.8$ GPa. The two spectra acquired for $\sigma_{TS} = 4.8$ GPa Dyneema[®] fiber are depicted in Fig. 5.36a,b. Taking the difference between them, the signal coming only from the intermediate component can be extracted (Fig. 5.36c)

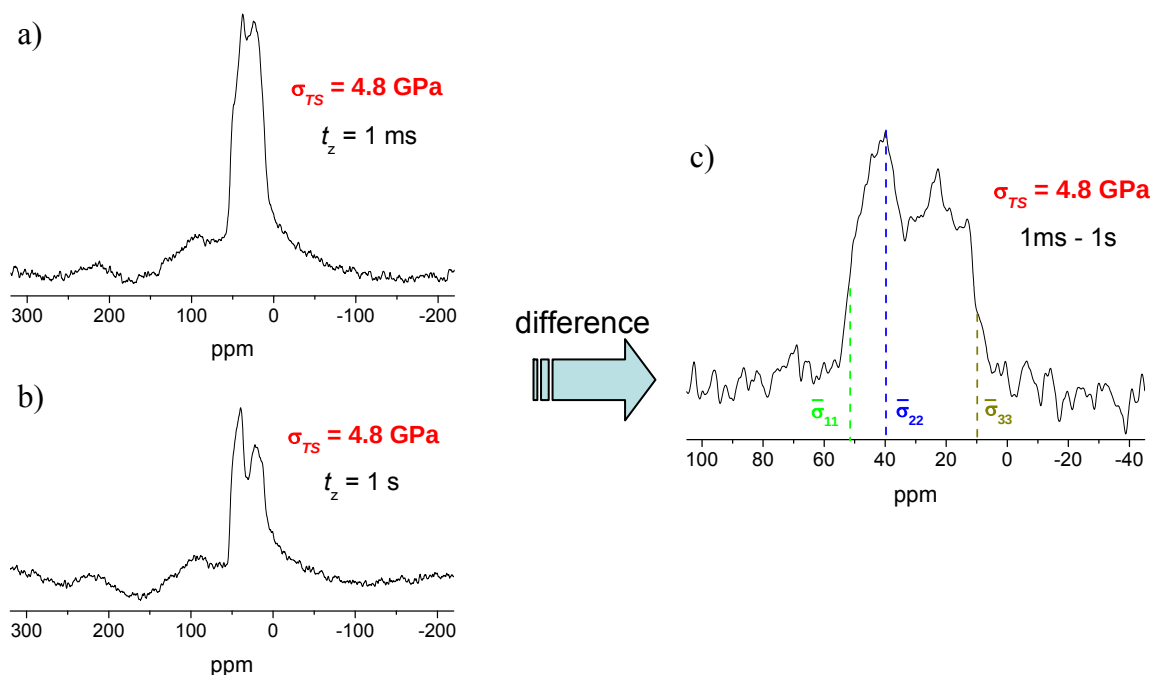


Fig. 5.36 ^{13}C $T_{1\rho}$ filtered spectra in powder-like Dyneema[®] fibre with $\sigma_{TS} = 4.8$ GPa, for different filter times: a) $t_z = 1$ ms and b) $t_z = 1$ s. c) The difference-spectrum showing two maxima is made only from the contributions of the intermediate component. The principal values of the motionally averaged chemical shift tensor $\bar{\sigma}_{11}$, $\bar{\sigma}_{22}$ and $\bar{\sigma}_{33}$ are also presented.

In order to investigate the motions inside the chains of the intermediate component we make use of the principal values of the motionally averaged chemical shift tensor $\bar{\sigma}_{11}$, $\bar{\sigma}_{22}$ and $\bar{\sigma}_{33}$. The directions of the principal values of motionally averaged chemical shift tensor are taken as shown in Fig. 5.37: $\bar{\sigma}_{33}$ is along the polymer chain axis, $\bar{\sigma}_{22}$ is along the bisector of the $^1\text{H} - ^{13}\text{C} - ^1\text{H}$ angle and $\bar{\sigma}_{11}$ is perpendicular to the $\bar{\sigma}_{22}$ and $\bar{\sigma}_{33}$ plane. The CH_2 groups in the intermediate component rotate about the polymer chain axis ($\bar{\sigma}_{33}$ direction) and the amplitude of this oscillation is evaluated. Actually both ^1H atoms can rotate independently about the chain axis with an angle Φ , so what is calculated further on is an average value $\langle \Phi \rangle$ of this rotational angle.

In general, fast motions around the chain axis manifest themselves by a reduced difference between the two perpendicular principal values $\bar{\sigma}_{11}$ and $\bar{\sigma}_{22}$ of the motionally

averaged chemical shift tensor. They are related to the rigid-limit values σ_{11} , σ_{22} and the rotation angle Φ according to [Sch2]:

$$\bar{\sigma}_{11} = -(1/2)\{\sigma_{33} - \sigma_{iso} - (\sigma_{11} - \sigma_{22})\langle\cos(2\phi)\rangle\} + \sigma_{iso} \quad (5.17a)$$

$$\bar{\sigma}_{22} = -(1/2)\{\sigma_{33} - \sigma_{iso} + (\sigma_{11} - \sigma_{22})\langle\cos(2\phi)\rangle\} + \sigma_{iso} \quad (5.17b)$$

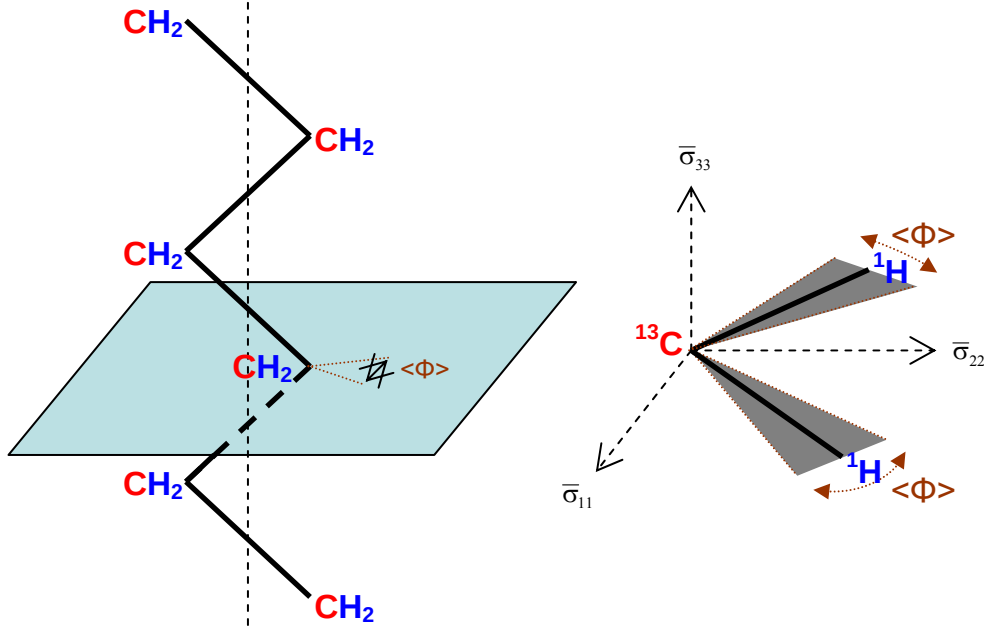


Fig. 5.37 Methylene average rotational angle around the chain axis from ^{13}C $T_{1\rho}$ filtered spectra of the intermediate fraction in the powder-like Dyneema[®] fibre with $\sigma_{TS} = 4.8$ GPa. The direction of the $\bar{\sigma}_{33}$ principal value of the motionally averaged chemical shift tensor is taken along the polymer chain axis, $\bar{\sigma}_{22}$ is chosen as the bisector of the $^1\text{H} - ^{13}\text{C} - ^1\text{H}$ angle and $\bar{\sigma}_{11}$ is perpendicular to the $\bar{\sigma}_{22}$ and $\bar{\sigma}_{33}$ plane.

From the above equations, as a result:

$$\langle\cos(2\phi)\rangle = \frac{\bar{\sigma}_{11} - \bar{\sigma}_{22}}{\sigma_{11} - \sigma_{22}} \quad (5.18)$$

Having given the rigid-limit values $\sigma_{11} = 50.1$ ppm and $\sigma_{22} = 36.5$ ppm [Tzo2] for polyethylene and extracting from our difference-spectrum the motionally averaged values $\bar{\sigma}_{11} = 51.8$ ppm and $\bar{\sigma}_{22} = 39.8$ ppm, according to the Eq. 5.18 we have computed the value of the methylene group average rotational angle as $\langle\phi\rangle = 14^\circ$ for the intermediate component of the Dyneema[®] fiber with $\sigma_{TS} = 4.8$ GPa. This should be compared with the 6° rotational motion amplitude occurring even in the cores of PE crystallites at ambient temperature [Hen1] and the 18° value obtained by Schmidt-Rohr et al. for cold-drawn HDPE with draw ratio $\lambda > 16$ [Mow1]. Note that fast chain flips by 180° would leave the chemical shift tensor invariant, but would reduce the long-range $^1\text{H} - ^1\text{H}$ dipolar couplings [Hu1].

5.3.9 Voids size by thermally polarized ^{129}Xe NMR

Many macroscopic properties such as glass transition, elastic modulus, and gas permeability of polymer materials that include UHMWPE fibers are related to the nature of the free volume (defects, voids) which is formed in the structure of the polymer [Tur1, Hig1]. Moreover, it was discussed recently that nanometer voids prevent crack growth in polymeric materials [Dut1]. Following the success of the positron annihilation and ^{129}Xe NMR as sensitive probes for the cavity space in microporous solids such as zeolites and clathrates, these techniques have recently been applied to elucidate the microscopic properties of the free volume in polymers [Nag1 and references therein].

Xenon-129 NMR spectra were measured at room temperature for UHMWPE Dyneema[®] fibers drawn with different values of the tensile strength σ_{TS} . As an example, two such spectra are shown in Fig. 5.38 for $\sigma_{TS} = 1.56$ GPa (a) and $\sigma_{TS} = 4.8$ GPa (b). The intense resonance was assigned to the free ^{129}Xe gas and set as a reference line at 0 ppm, whereas the weak resonance shifted downfield at about 190 ppm was assigned to the ^{129}Xe atoms inside the fibers.

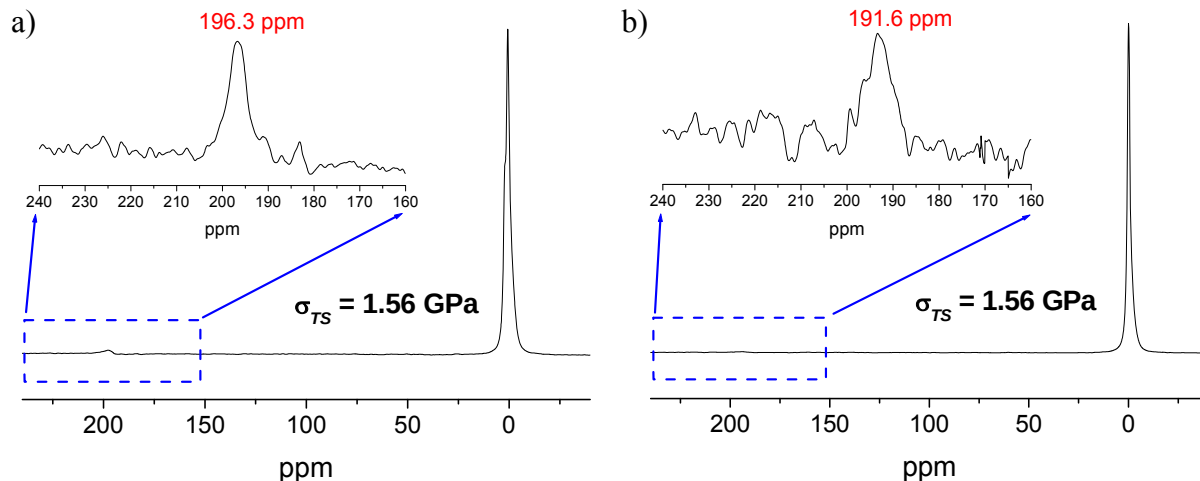


Fig. 5.38 Xenon-129 NMR spectra at 20 bar xenon pressure for UHMWPE fibers with a) $\sigma_{TS} = 1.56$ GPa and b) $\sigma_{TS} = 4.8$ GPa.

Some qualitative results are evident: (i) the number of the xenon atoms penetrating the UHMWPE fibers is about one order of magnitude smaller than the number of xenon atoms in the free gas. As in many other polymers, the xenon gas penetrates mainly in the amorphous domains and enters the voids. No asymmetry of the resonances is detected showing that ^{129}Xe explores a quasi-isotropic environment. Therefore, the total volume of the voids (defects) or free volume explored by ^{129}Xe is expected to be relatively small compared to the total volume

of the fiber; (ii) the position and the width of the xenon resonance around 190 ppm are functions of tensile strength.

The dependence of the ^{129}Xe chemical shift on σ_{TS} is shown in Fig. 5.39. A clear trend of the change in the chemical shift upfield, i.e., toward the chemical shift value of free xenon gas, is detected. We can conclude that the volume explored increases and the probability of Xe atoms collisions with the void surface becomes higher (see below).

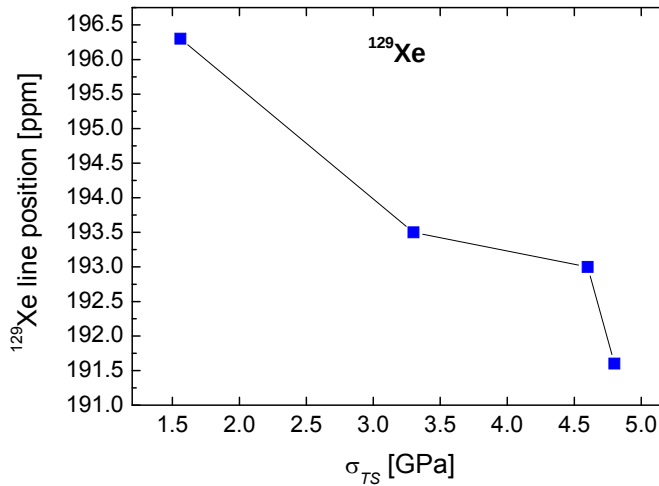


Fig. 5.39 The dependence of the ^{129}Xe chemical shift on the tensile strength for UHMWPE Dyneema[®] fibers.

The dependence of the linewidth at the half-intensity ($\Delta\nu_{1/2}$) of ^{129}Xe resonances around 190 ppm on tensile strength for UHMWPE fibers is shown in Fig. 5.40. An increase in $\Delta\nu_{1/2}$ with tensile strength is detected, with some deviation for the sample with $\sigma_{TS} = 4.6$ GPa. As before we can conclude that the void size increases with σ_{TS} due to the increase in the surface of the voids and the enhancement of the xenon atoms collisions with these surfaces. This mechanism of line broadening it is well known for the relaxation in gases [Abr1].

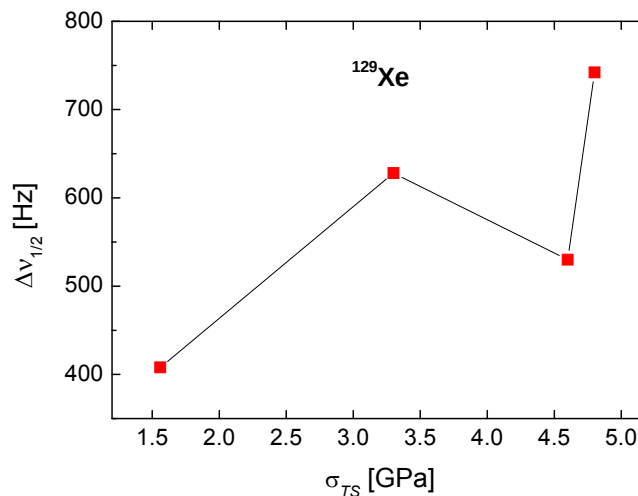


Fig. 5.40 The dependence of the full linewidth at the half-intensity ($\Delta\nu_{1/2}$) of ^{129}Xe resonances around 190 ppm on tensile strength for UHMWPE Dyneema[®] fibers.

Void sizes from ^{129}Xe chemical shift in drawn UHMWPE fibers using a theoretical approach. The chemical shift of ^{129}Xe atoms absorbed in polymers is a sensitive detector for the pore size. It can be expressed, in general, by a linear combination of four terms, as shown by Ito and Fraissard [Fra1],

$$\delta = \delta_0 + \delta_s + \delta_{\text{Xe-Xe}}\rho + \delta_E, \quad (5.19)$$

where δ_0 denotes the chemical shift value of gaseous ^{129}Xe at zero density, δ_s and $\delta_{\text{Xe-Xe}}$ are the chemical shift originating from the collisions between xenon atoms and the wall of the cavity and from Xe-Xe collisions, respectively. The density of the xenon atoms in the voids is denoted by ρ ; δ_E represents the contribution due to polarization of xenon atoms by the finite electric field from ionic species in the cavity, but can be neglected in polymers. Assuming that ^{129}Xe atoms collisions are the same inside the pores and in free gas and that δ_0 represents our 0 ppm reference corresponding to the free Xe gas peak, only δ_s remains in the right side of Eq. (5.19) and it should be a characteristic parameter of the void size in the polymer.

Demarquay and Fraissard [Fra2] succeeded to develop a theoretical framework that quantitatively relates the parameter δ_s with the mean free path of the xenon atoms in the voids. The basic assumption is that the value δ_s is the average of the xenon shift in rapid exchange between a position on the inner surface of the pore and a position inside of the pore. The following relationship was established between δ_s and the mean free path $\bar{l}$,

$$\delta_s = 243 \frac{2.054}{2.054 + \bar{l}} \quad [\text{ppm}] \quad (5.20)$$

The numerical constants were established based on the xenon adsorbed on dealuminated zeolite [Fra2]. For this material the chemical shift of ^{129}Xe is 243 ppm. The mean free path $\bar{l}$ was related to the pore diameter D_{pore} by the relationship

$$\bar{l} = \frac{1}{2}(D_{\text{pore}} - D_{\text{Xe}}) \quad [\text{nm}], \quad (5.21)$$

where the diameter of the xenon atom is $D_{\text{Xe}} = 0.44$ nm. Finally, we can write from the above equations

$$\delta_s = \frac{49.9122}{0.5D_{\text{pore}} - 0.0146} \quad [\text{ppm}] \quad (5.22)$$

Based on Eq. 5.22, the values of δ_s as a function of D_{pore} in nm are represented in Fig. 5.41. Only the region of interest for us is shown in this figure, where a linear dependence of the measured chemical shift $\delta_{\text{measured}} = \delta_s = \delta_{\text{total}} - \delta_0 - \delta_{\text{Xe-Xe}}\rho$ on D_{pore} is evident. From the Eq. 5.22, for the UHMWPE fibre with $\sigma_{\text{TS}} = 1.56$ GPa, we calculated $D_{\text{pore}} = 0.537$ nm ($\delta_s =$

196.3 ppm) and for $\sigma_{TS} = 4.6$ GPa, $D_{\text{pore}} = 0.55$ nm ($\delta_s = 191.6$ ppm). So the void size increases with σ_{TS} .

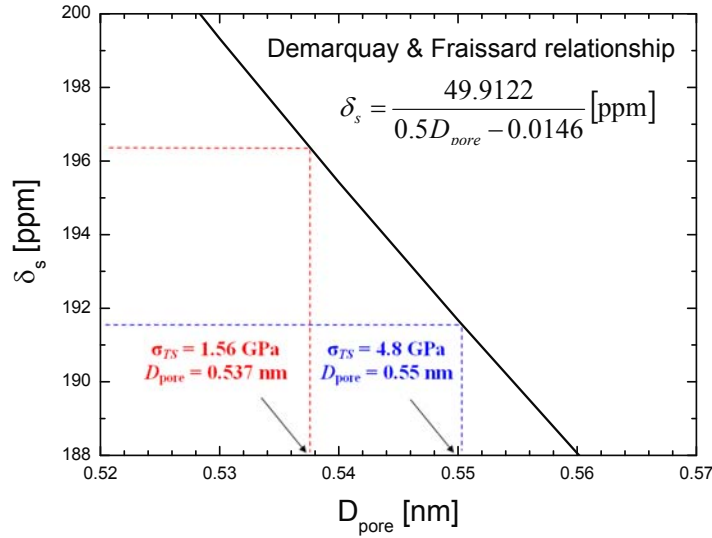


Fig. 5.41 The dependence of the measured chemical shift δ_s of ^{129}Xe resonances on the pore size diameter D_{pore} following Eq. 5.22.

Using this theoretical approach, the dependence of D_{pore} on tensile strength σ_{TS} for UHMWPE Dyneema[®] fibers is shown in Fig. 5.42. So D_{pore} depends, in the limits of the experimental errors, quasi-linearly on tensile strength for the investigated range of σ_{TS} .

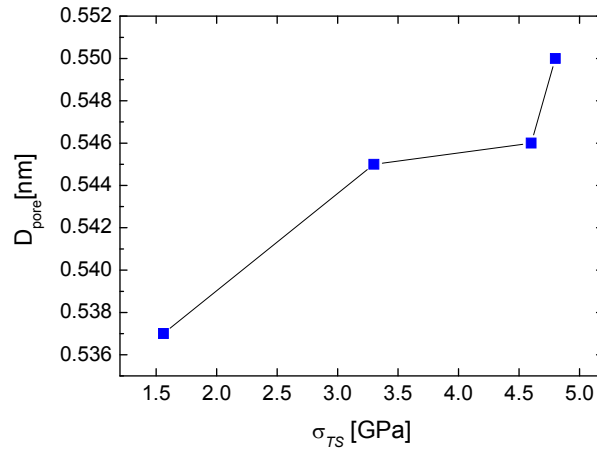


Fig. 5.42 The dependence of the diameter of voids on σ_{TS} for drawn UHMWPE Dyneema[®] fibers.

Void sizes from ^{129}Xe chemical shift in drawn UHMWPE fibers using an experimental calibration curve. Another independent method from which we can estimate the void sizes is based on a calibration curve that establishes a correlation between the radius of the voids and the measured chemical shift. An example of such a calibration curve is shown in Fig. 5.43 where the point (1) correspond to voids in solid Xe at 21 K, point (2) is related to solid Xe at 160 K, and points (3)-(7) were measured for dodecasil-3C with different pore sizes [Rip1].

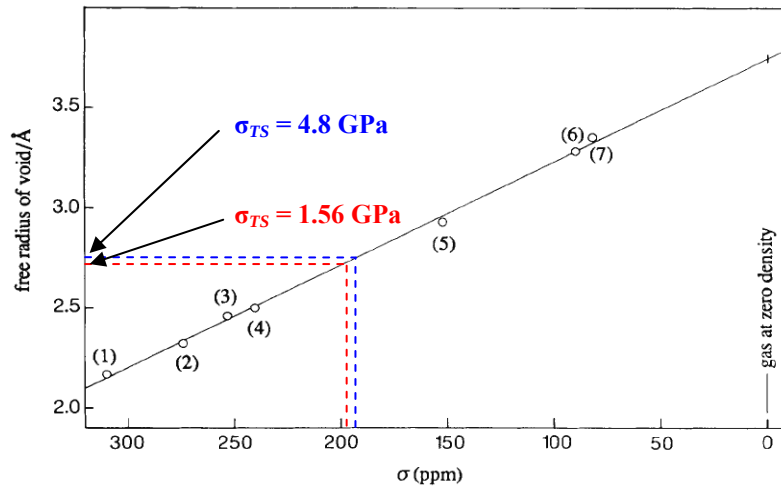


Fig. 5.43 The dependence of the void radius on the measured chemical shift of ^{129}Xe resonances.

Having already measured the values of the ^{129}Xe chemical shift for our series of samples and using this experimental calibration curve, the following values of the voids sizes have been obtained: for $\sigma_{TS} = 1.56$ GPa sample, $D_{\text{pore}} = 0.54$ nm and for $\sigma_{TS} = 4.8$ GPa sample, $D_{\text{pore}} = 0.55$ nm. These pore sizes are in a very good agreement with those obtained from the Demarquay and Fraissard relationship.

So we can remark that the void size (or free volume) of the Dyneema[®] UHMWPE in the amorphous and intermediate fractions are relatively small and contains on the average only one Xe atom with the diameter of 0.44 nm. Both our approaches, the theoretical one and the experimental one, assume only the presence of spherical voids, which can be compared just in a first order approximation with the reality. Due to the uniaxial mechanical deformation of the UHMWPE the existence of elongated pores cannot be excluded. This should be an interesting investigation topic for the future.

5.4 Conclusions

The morphological structure of drawn semicrystalline polymers is more complex than can be described by a simple two-phase model. Using ^1H NMR spectroscopy three phases with different concentrations were detected for Dyneema[®] fibers with small values of tensile strength. At larger values of tensile strength, i.e. for $\sigma_{TS} \geq 2.9$ GPa the concentration of interface and mobile fraction is almost the same, of the order of 1 %. A large change in the phase composition of Dyneema[®] fiber with $\sigma_{TS} = 2.5$ GPa was detected due to changes in the processing temperature. The accuracy of the data is affected by the approximate

deconvolution procedure of the ^1H wide-line NMR spectra. Nevertheless, the measured trend is correct and reflects the actual modification of phase composition under the drawing process. Different procedures to improve the determination of the spectral components are proposed.

The ^1H NMR spectral contrast is enhanced by the measurements made at higher temperature, in our case of 70°C . As expected the fiber orientation affects strongly the ^1H NMR signal. A disordered sample was prepared and the results shown to be independent of the fiber size. The Dyneema[®] fibers have a heterogeneous composition tested by ^1H NMR under MAS. The large increase in the crystalline phase packing was measured from second and fourth van Vleck moments. The chain dynamics is strongly affected by the drawing process. A constant increase in the polymer chain immobilization was detected for the rigid fraction. The chain dynamics of the Dyneema[®] fibers with $\sigma_{TS} = 1.56$ GPa and $\sigma_{TS} = 2.5$ GPa are strongly different. The chain dynamics of the interface and mobile fraction is almost the same for samples with $\sigma_{TS} \geq 2.9$ GPa. An editing ^1H NMR experiment was introduced to record only the mobile fraction signal of Dyneema[®] fibers. Unfortunately, the contrast in chain dynamics, investigated by means of the linewidth of the edited spectra, proves to be not very high at least for the delayed acquisition time of $50\ \mu\text{s}$ used in this case.

The changes of the domain sizes for crystalline and mobile phases for drawn Dyneema[®] fibers were measured by ^1H spin-diffusion experiments. A simplified 1D morphological model was considered in order to increase the accuracy of the analysis. A strong change (from 50 nm to 250 nm) in the rigid domain size is detected for highly drawn fibers. The mobile domain size slightly increases with σ_{TS} (from 1.3 nm to 2 nm). This could be related to an increase in the number of defects (probably voids) of highly drawn Dyneema[®] fibers.

The next step will be to use a 2D morphological model and to combine DQ and Goldman-Shen dipolar filters for a more accurate evaluation of the domain sizes. The NMR results should be compared with X-ray scattering investigation. At this stage we do not have access to the domain sizes measured from X-ray scattering.

By a series of ^{13}C NMR experiments, of which several utilize an “inverse ^{13}C T_1 filter” that enables a selective observation of the signals of the various components, the morphological structure, the characteristic molecular conformation and the mobility of the intermediate component(s) has been examined. For the first time a ^{13}C investigation of the fraction composition and chain mobility has been done for UHMWPE in such a broad range of tensile strengths, where a partially mobile and disordered all-trans fraction was detected. This fraction represents the second largest component in the system (up to 30% for the

Dyneema[®] sample with $\sigma_{TS} = 1.56$ GPa), ahead of the amorphous and the monoclinic crystalline phases. The content of the intermediate fraction is decreasing dramatically as a function of tensile strength and the intermediate component chain segments undergo intermediate-amplitude motions.

The chain packing density (chain order) for intermediate fraction increases with σ_{TS} for Dyneema[®] fibres, based on the dependence on tensile strength of the ^{13}C isotropic chemical shift and of the linewidth of the ^{13}C $T_{1,\text{C}}$ edited spectra.

The average rotational angle of the methylene group around the chain axis can be measured from the ^{13}C $T_{1,\text{C}}$ edited spectra. This angle of 14° is 1.3 times smaller for the Dyneema[®] fibre with $\sigma_{TS} = 1.56$ GPa as compared to cold-drawn HDPE with draw ratio $\lambda > 16$ investigated by K. Schmidt-Rohr et al. [Mow1].

NMR of thermally polarized ^{129}Xe can reveal the existence of voids (free volume) in UHMWPE fibers. The pore sizes of UHMWPE fibers can be measured using two independent methods using the ^{129}Xe chemical shift. The average size of the pores with assumed spherical symmetry is of the order of 0.54 nm and increase with σ_{TS} . This result is in agreement with that based on the dependence of the spectral linewidth and ^{129}Xe chemical shift on σ_{TS} .

The amount of in-polymer-penetrating xenon atoms is relatively low and it takes several days until the equilibrium is established with the gas at 20 bar. Moreover, the long T_1 relaxation time and the low NMR sensitivity of ^{129}Xe lead to long acquisition time of more than one day. By using continuous flow hyperpolarized ^{129}Xe it should be possible to measure a NMR spectrum in just one shot, but unfortunately the information about the fiber volume would be lost due to the long penetration time and the loss of polarization. Nevertheless, the existence of the fiber defects at the surface could be investigated.

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6 Ultrafast ^1H and hyperpolarized ^{129}Xe multidimensional NMR spectroscopy

6.1 Introduction

Few analytical techniques in science match, in either breadth or depth, the impact achieved by nuclear magnetic resonance (NMR) [Gra1]. After establishing itself as a tool for the characterization of organic molecules [Pop1], the use of NMR has spread throughout the decades, reaching into areas as diverse as pharmaceuticals, metabolic studies, structural biology, solid state chemistry, condensed matter physics, rheology, medical diagnosis (where it is known as MRI), and more recently neurobiology [Bro1, Bux1, Cal1, Cav1, Coh1, Sch2]. Lying at the core of the expansion of NMR are powerful protocols developed over the years for characterizing the nuclear spin environment; in particular, the Fourier transform (FT) and the multidimensional method of NMR analysis [Ren1, Jee1, Aue1]. Contemporary NMR applications in all the scientific disciplines mentioned above rely routinely on Fourier and multidimensional spectroscopy for their implementation.

Unidimensional Fourier spectroscopy brings the so-called multiplex advantage into NMR, enabling a shortening in the data-scanning time by orders of magnitude and bringing about a concomitant increase in the signal-to-noise ratio (S/N) achievable per unit time. FT-NMR methods, the principles of which eventually extended to many other forms of spectroscopy [Mar1], encode the complete spectral distribution $I(\nu)$ being sought by acquiring a single time-domain transient $S(t)$, from which $I(\nu)$ is reconstructed via a discrete version of the FT calculation $I(\nu) = (1/2\pi) \int_0^{AqT} S(t) e^{-i\nu t} dt$. By contrast, the goal of multidimensional spectroscopy is not just to measure but to correlate NMR frequencies over several spectral dimensions. For instance in 2D NMR, the scheme [Aue1]

$$\text{preparation} - \text{evolution} (t_1) - \text{mixing} - \text{acquisition} (t_2) \quad (6.1)$$

provides a time-domain set $S(t_1, t_2)$, from which correlations between frequencies during the evolution and acquisition periods can be extracted as

$$I(\nu_1, \nu_2) = \int_0^{AqT_1} \int_0^{AqT_2} S(t_1, t_2) e^{-i\nu_1 t_1} e^{-i\nu_2 t_2} dt_1 dt_2. \text{ Collecting the 2D } S(t_1, t_2) \text{ NMR data set over}$$

sufficiently large regions of the time domain is usually carried out by a parametric increment of t_1 in N_1 steps of duration Δt_1 , followed by a conventional t_2 acquisition in dwell times Δt_2 . The extent of the sampling along the t_1 and t_2 domains eventually determines the line shapes of the final 2D NMR peaks: their so-called point-spread functions. Obtaining purely absorptive 2D NMR line shapes usually demands the collection of complementary data sets consisting of several N_1 points [Ern2, Kes1]; because each of these points constitutes an independent signal acquisition, 2D NMR reduces to some extent the original ability of 1D FT NMR to retrieve a complete spectrum within a single scan. Indeed, even in cases where the S/N is outstanding, 2D NMR experiments still may demand the acquisition of hundreds of transients to sample the t_1 domain adequately. This complication is compounded further in higher dimensional NMR.

The relatively slow multi-scan approach of multidimensional FT spectroscopy was found particularly confining in 2D MRI. Yet, in this case, the availability of intense signals combined with an unparalleled flexibility available for manipulating the MRI interactions enabled the eventual development of fast multidimensional acquisition techniques [McK1 and references therein]. Principal among these techniques is echo planar imaging (EPI), which fully expands the multiplex advantage of FT NMR into several dimensions [Ste1]. Only rarely, however, could the principles underlying EPI be exported directly into high-resolution NMR spectroscopy [Bax1, Blu1, Fry1].

Driven in part by the constraint of longer times associated to experiments with increasing dimensionalities, recent years have witnessed the emergence of alternatives capable of speeding up the acquisition of 2D NMR data [Kup1, Atr1], including so-called “ultrafast” approaches capable of completing arbitrary n D NMR experiments within a single-scan [Fry2, Fry3]. Such proposal endows different spin-packets within a resonance that has been subject to an inhomogeneous broadening, with the equivalent of different increments in their indirect-domain time evolutions. Although when dealing with solids it is conceivable to rely on the anisotropic character of spin interactions to impart such inhomogeneous broadening [Bha1], the most straightforward way of doing this is by applying suitably-refocused linear gradient fields $\mathbf{G} = G_0 \mathbf{g}$, imposing different frequencies on different positions within the sample. A train of frequency-incremented or frequency-chirped radiofrequency (RF) pulses can then be used to excite, refocus or store the spins evolution progressively as a function of their spatial positions. This imposes a spatial winding on the spins magnetization $\mathbf{M}$ that parallels the gradient $\mathbf{g}$ geometry, whose magnitude is controlled by the indirect-domain $I(\Omega_1)$ spectrum one is attempting to measure according to

$$M(r) \approx \sum_{\Omega_1} I(\Omega_1) \exp(iC\Omega_1 r) \quad (6.2)$$

where Ω_1 represents the spins chemical shift and C is a parameter under experimental control. Unlike conventional time-domain procedures, this imprinting can be implemented over the full desired range $0 \leq t_1 \leq t_1^{\max}$ of evolution times within a single-scan. Such spatially encoded information will be coherently preserved throughout the sequence mixing process, and can be subsequently read-out by a G_a acquisition gradient possessing the same geometry as its encoding counterpart. When such gradient is applied, spins become subject to the action of an additional acquisition wavenumber $k(t) = \gamma_a \int_t G_a(t') dt'$, leading to signals that when integrated over the sample length L

$$\begin{aligned} S[k(t)] &\approx \sum_{\Omega_1} I(\Omega_1) \int_L \exp[iC\Omega_1 r] \exp[ik(t)r] dr \\ &\approx \sum_{\Omega_1} I(\Omega_1) \delta[C\Omega_1 + k] \end{aligned} \quad (6.3)$$

read-out the indirect-domain frequency spectrum $I(\Omega_1)$ as echoes along the k/v_1 frequency axis – no Fourier transformations involved.

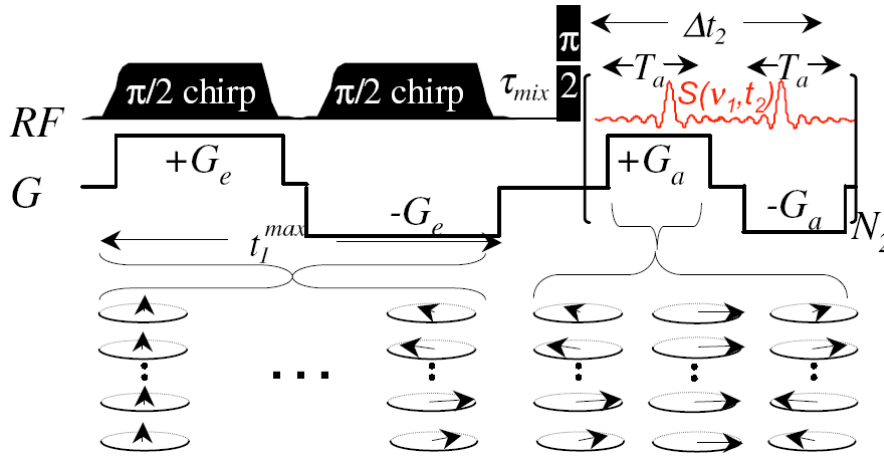


Fig. 6.1 Single-scan 2D NOESY-type sequence assayed throughout this study. The first two chirped RF pulses carry a spatial encoding of the indirect-domain interactions, while the oscillating $\pm G_a$ gradients do a repetitive read-out of their $I(\Omega_1)$ spectra as a function of time t_2 .

Moreover the times T_a over which G_a needs to be applied are fairly short; suffice it to make $k_{\max} = \gamma_a G_a T_a$ equal to the spectral window SW_1 to be explored, scaled by the $C \approx t_1^{\max}/L$ coefficient, leading to $T_a \approx t_1^{\max} \cdot \text{SW}_1 / (\gamma_a G_a L)$ of a few 100's of μs . This interval is much shorter than common T_2 decays, implying that the G_a -driven read-out process can be done and undone numerous times over the course of a single acquisition. Such repeated oscillations will

generate a train of k/Ω_1 - echoes, modulated as a function of the direct-domain evolution frequencies Ω_2 acting during the course of t_2

$$S[k(t_2), t_2] = \sum_{\Omega_2} \sum_{\Omega_1} I(\Omega_1, \Omega_2) \delta[C\Omega_1 + k] \exp(i\Omega_2 t_2) \quad (6.4)$$

Fourier transformation of the resulting $S[k(t_2), t_2]$ array against t_2 will thereby provide the 2D $I(\Omega_1, \Omega_2)$ NMR spectrum being sought – still, while confined within a single-scan. The general scheme for an amplitude-modulated ultrafast NOESY-type sequence is shown in Fig. 6.1, where a bipolar encoding gradient acting in synchrony with two identical $\pi/2$ RF sweeps [Shr1] is used.

While the principles of the ultrafast multidimensional NMR spectroscopy were demonstrated at Weizmann Institute of Science, Israel (Prof. Frydman's group) for a range of organic and biomolecular samples in the liquid phase, they have not to our knowledge been hitherto reported on solid samples undergoing MAS. Implementing of the ultrafast technique at Institute for Technical and Macromolecular Chemistry Aachen and analyzing the novel aspects that may arise in solids spinning-case scenario constitutes the main aim of this work.

6.2 Experimental

Conventional and single-scan 2D ^1H NMR experiments were acquired on liquid (ethanol ($\text{CH}_3\text{-CH}_2\text{-OH}$) and n-butylchloride ($\text{CH}_3\text{-(CH}_2\text{)}_3\text{-Cl}$)) and rubber samples, using two complementary setups.

One of these setups involved a Bruker DSX 500 NMR spectrometer ($B_0 = 11.75$ T), operating at 500.44 MHz ^1H resonance frequency. A gradient-enhanced 4 mm solid-state MAS probe was used, providing a fixed gradient orientation along the rotor's axis with strengths of up to 50 G/cm and spinning rates up to 15 kHz. Using this setup, conventional and ultrafast NOESY and INADEQUATE experiments were performed. The scheme describing the conventional 2D NOESY experiment is shown in Fig. 6.2. The measurement was made at ambient temperature ($T = 295$ K) under fast magic angle sample spinning of 10 kHz. The 90° ^1H pulse length was 5.5 μs at 6 dB power attenuation. A number of 128 increments of the t_1 evolution period was used. The mixing time employed was 30 ms and the recycle delay 3 s.

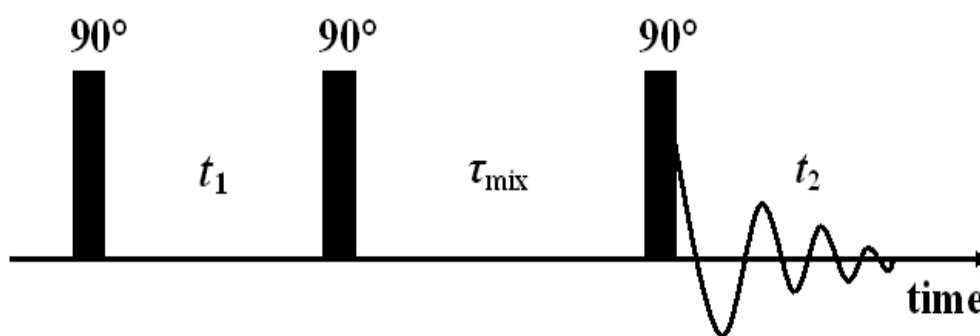


Fig. 6.2 Conventional 2D NOESY/EXSY pulse scheme.

The scheme describing the ultrafast NOESY experiment is presented in Fig. 6.1. The chirp pulses swept 100 kHz in 10 ms at 40 dB power attenuation. The value of the excitation gradient was $G_e = 14$ G/cm, whereas the acquisition gradient was $G_a = 40$ G/cm. A number of $N_2 = 64$ positive-negative gradient switchings was used in the acquisition, where $T_a = 400$ μs (see Fig. 6.1). A 400 μs purging gradient pulse (P) of 14 G/cm was applied just prior to the beginning of the data digitization.

The figure 6.3 shows the single-scan 2D homonuclear INADEQUATE-based double-quantum (DQ) ^1H NMR pulse sequence scheme used in this study. In order to excite the DQ coherences, the pulse sequence begins with a spin-echo sandwich with duration τ (chosen to match the $J_{\text{H-H}}$ coupling constant, according to the relation $\tau = |(2J)^{-1}|$). The length of the 90° and 180° hard pulses being 6.5 μs and 13 μs , respectively with a power attenuation of 6 dB.

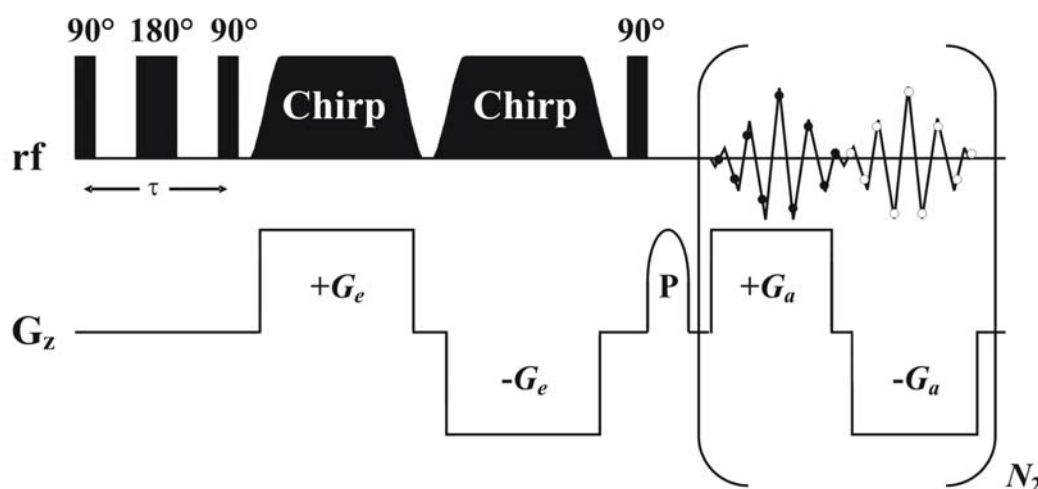


Fig. 6.3 The pulse scheme involved in the collection of 2D DQ filtered NMR spectra within a single-scan.

The chirp pulses swept 90 kHz in 2 ms at 14 dB power attenuation. The excitation and acquisition gradients were $G_e = 19$ G/cm and $G_a = 38$ G/cm, respectively. The acquisition involved $N_2 = 64$ gradient echoes, T_a being 600 μs (gradient pulses of 500 μs and gradient-switching times of 100 μs), sampled with a constant dwell time of 2 μs . A 400 μs purging

gradient pulse (P) of 13 G/cm was applied just prior to the beginning of the data digitization. The acquired data points were separated for their off-line processing into $+G_a$ and $-G_a$ contributions and subjected to a suitable shearing, zero-filling to 128×256 (k, t_2)-points, Fourier transformation against t_2 , and magnitude mode calculation.

The second setup used in this work involved a 7.1 T microimaging scanner, equipped with a multi-axis (G_x, G_y, G_z) accessory capable of delivering up to 100 G/cm gradients along three orthogonal directions. This allowed us to orient the secular components of the magnetic field gradient $\vec{G} = \vec{\nabla}B_z = G_0\hat{g}$ at arbitrary orientations versus the axis of sample rotation. A narrow-bore probehead equipped with a 2.5 mm spinner capable of executing MAS at rates up to 35 kHz was then stripped away from its normal casing, shielded with aluminum foil to reduce eddy currents while minimizing RF interferences, and installed within this gradient set. An important component of the tests carried out using this setup required finding the MAS rotor orientation within the $\vec{\nabla}B_z$ gradient frame. A reliable way for doing so was found by arraying a simple gradient-echo experiment with fixed timing and gradient strength $G_0 = \sqrt{G_x^2 + G_y^2 + G_z^2}$ over a range of $G_x/G_y/G_z$ combinations, corresponding to a full exploration of the $\hat{g}$ orientation over the solid sphere (Fig. 6.4). The resulting images consist of a series of 1D profiles whose intensities peak over a characteristic, well-defined band of values (Fig. 6.5) corresponding to $\hat{g}$ orientations that are normal to the rotor's long cylindrical axis. A spherical representation of these values defines then a single central azimuth point $(\theta_{\text{rot}}, \phi_{\text{rot}})$, orienting the MAS spinning axis within the laboratory frame defined by the orthogonal gradient set (Fig. 6.6).

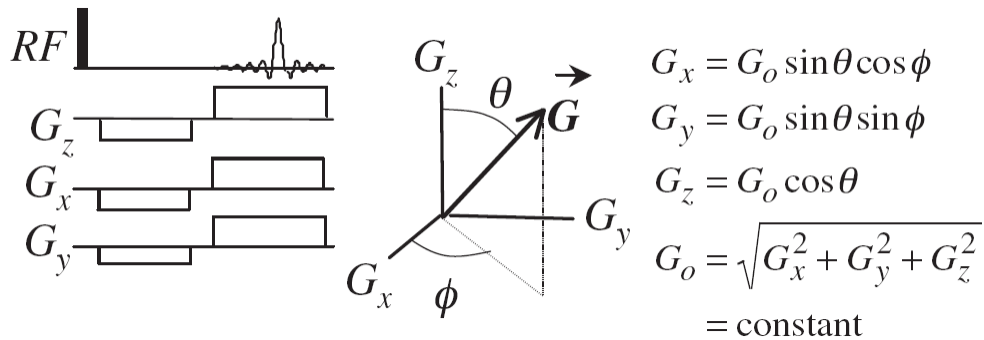


Fig. 6.4 Strategy employed to find the exact $(\theta_{\text{rot}}, \phi_{\text{rot}})$ orientation of the MAS rotor, within a laboratory frame defined by the three orthogonal components of a magnetic field gradient set. A gradient-echo pulse sequence is arrayed, given by a constant overall G_0 gradient strength but varying the (G_x, G_y, G_z) components, defining different (θ, ϕ) angles within a laboratory frame.

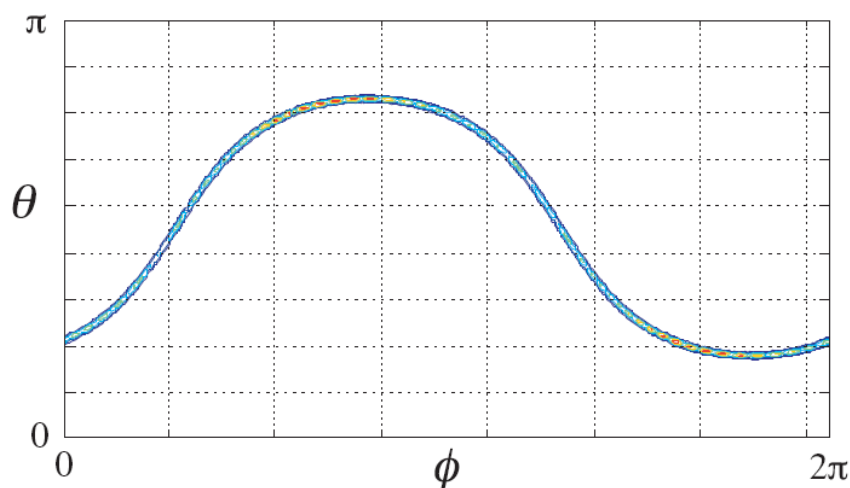


Fig. 6.5 Using the pulse scheme from Fig. 6.4 and changing the resulting polar and azimuthal angles yields an array of 1D sample profiles, whose area is constant but width is minimal when the gradient orientation $\hat{g}$ is normal to the rotor axis.

A more practical yet essentially equivalent way to retrieve this desired orientation consists of looking first for the normal to the rotor axis within the (G_x, G_y) plane by finding the sharpest profile arising for a fixed G_0 value while keeping $G_z = 0$; with ϕ_{rot} 's value thus defined, the sharpest profile obtained as a function of different G_z components enables an unambiguous determination of θ_{rot} . The rotor axis could thereby be defined using two rapid 1D searches (instead of a full 2D one) prior to each measurement on either liquids or solids; with this at hand it was feasible to explore the effects that misaligning $\hat{g}$ and the axis of MAS had on the acquisition of ultrafast 2D NMR data on rotating samples.

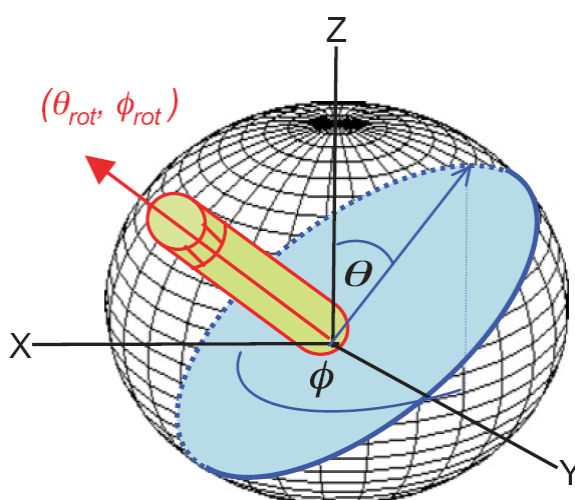


Fig. 6.6 Arraying the resulting (θ, ϕ) maximal values in a spherical representation yields a well-defined azimuth, providing an exact orientation of the rotor within the laboratory frame.

6.3 Ultrafast 2D ^1H NMR spectroscopy

In order to demonstrate both the overall principles as well as practical examples of the novel ultrafast 2D NMR approach, the ultrafast versions of the NOESY and 2D homonuclear INADEQUATE-based double-quantum ^1H NMR experiments have been firstly applied for two liquid samples, *n*-butylchloride and ethanol. Figure 6.7 shows the ultrafast 2D NMR spectrum of *n*-butylchloride, obtained using the amplitude-modulated exchange-type sequence from Fig. 6.1, implemented using a bipolar encoding gradient acting in synchrony with two identical $\pi/2$ RF sweeps on a high-resolution gradient-equipped MAS NMR probe. Just prior to beginning data digitization, in order to clean up undesired residual signals, a purging gradient pulse was applied, followed then by an oscillating $\pm G_a$ gradient for the sake of unraveling the nature of the pre- and post-mixing spin evolution frequencies. Data points were collected over the course of this $\pm G_a$ gradient application in the usual ultrafast NMR rapid-sampling fashion, and then sorted out according to their k/v_1 values and Fourier transformed as a function of t_2 in order to retrieve the desired 2D NMR spectrum.

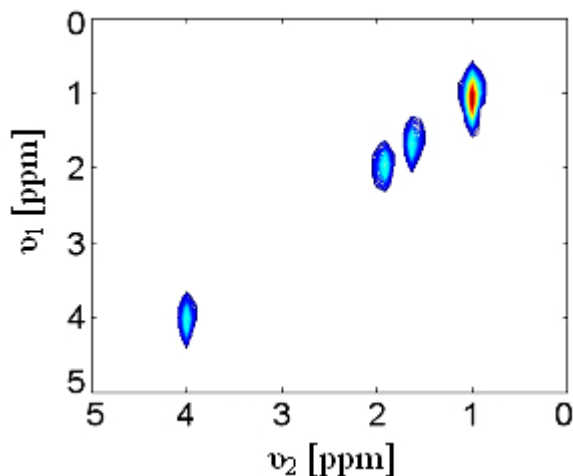


Fig. 6.7 Single-scan 2D NMR spectrum acquired upon executing the sequence in Fig. 6.1 on a liquid *n*-butylchloride sample, using a gradient-equipped MAS NMR probe (fixed gradient coil) under non-spinning conditions. Data were recorded at 11.7 T with $G_e = 14$ G/cm, chirp pulses sweeping 100 kHz over 10 ms, $\tau_{\text{mix}} = 100$ ms, $G_a = 40$ G/cm, $N_2 = 64$, $T_a = 400$ μs (gradient pulses of 350 μs , gradient-switching times of 50 μs , and a constant sampling time of 2 μs). A 400 μs purging gradient of 14 G/cm was applied just prior to the beginning of the data digitization. The acquired data points were separated for processing into $+G_a$ and $-G_a$ contributions; the plot illustrated here resulted from subjecting one of these sets to a suitable shearing, zero-filling to 128×256 (k , t_2)-points, Fourier transformation against t_2 , and magnitude mode calculation. The total experimental time was 0.3 s.

The “ultrafast” spectrum in Fig. 6.7 is in very good agreement with the conventional ones, with a loss in the sensitivity though. This is the main reason why the cross-peaks are under the limit of detection for the NOESY experiment carried out on this liquid sample even if the measurements have been repeated using 8 and 16 scans. However the quality and correctness of the 2D NMR data proves that the ultrafast procedure works properly.

The second experiment to be discussed involved the ultrafast version of the 2D homonuclear INADEQUATE-based double-quantum ^1H NMR acquisition on ethanol (Fig. 6.8). In order to excite the double-quantum coherences, the pulse sequence (Fig. 6.3) begins with a spin-echo sandwich (two pulses of 90° flip angle with a 180° flip angle pulse in between) with duration τ . The interval τ is chosen to match the $J_{\text{H-H}}$ coupling constant, according to $\tau = |(2J_{12})^{-1}|$. Almost immediately follows the first chirp pulse that produces an encoding of the indirect-domain spin evolution as a function of the z position in the sample, in the presence of a gradient $+G_e$. Further on comes the “storage” of the t_1 -encoded coherences applying the second chirp pulse while subjecting the spins to a reversed gradient $-G_e$. After this evolution, the double-quantum coherences are converted into observable (-1)-quantum coherences by the last 90° pulse. The data are collected then in the presence of an oscillating acquisition gradient $\pm G_a$, capable of repetitively unwinding and winding the shift-induced spiral of spin-packets encoded during the excitation.

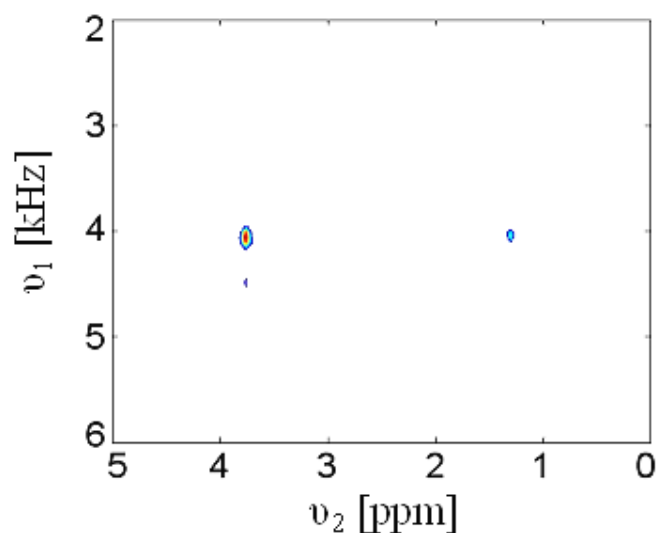


Fig. 6.8 Single-scan ^1H 2D DQ filtered NMR spectrum of ethanol using the following parameters: $G_e = 19 \text{ G/cm}$, $\Delta O = O_i - O_f = 90 \text{ kHz}$, length of the chirp pulses of 2 ms with a power attenuation of 14 dB, $G_a = 38 \text{ G/cm}$, $N_2 = 64$, $T_a = 600 \mu\text{s}$ (gradient pulses of $500 \mu\text{s}$ and gradient-switching times of $100 \mu\text{s}$) sampled with a constant dwell time of $2 \mu\text{s}$. A $400 \mu\text{s}$ purging gradient pulse (P) of 13 G/cm was applied just prior to the beginning of the data digitization. The length of the 90° and 180° hard pulses was $6.5 \mu\text{s}$ and $13 \mu\text{s}$ respectively, with a power attenuation of 6 dB. Total experimental time was 0.4s.

The total experimental time for the this two types of measurements was 0.3 s and 0.4 s respectively, the acquisition involving 64 N_2 gradient echoes, in comparison with the classical experiments which require about 4 h and 5 h respectively for 128 t_1 points in the indirect dimension and 64 scans.

The principles of the ultrafast 2D NMR method were applied afterwards for the investigation of soft solids, for instance elastomers. The measurements being done at 500 MHz ^1H resonance frequency, a good signal-to-noise is expected, so consequently, no problems in terms of sensitivity should appear. Moreover, the liquid-like behavior of elastomers under fast magic angle spinning conditions should be very well exploited by the ultrafast multidimensional NMR approach.

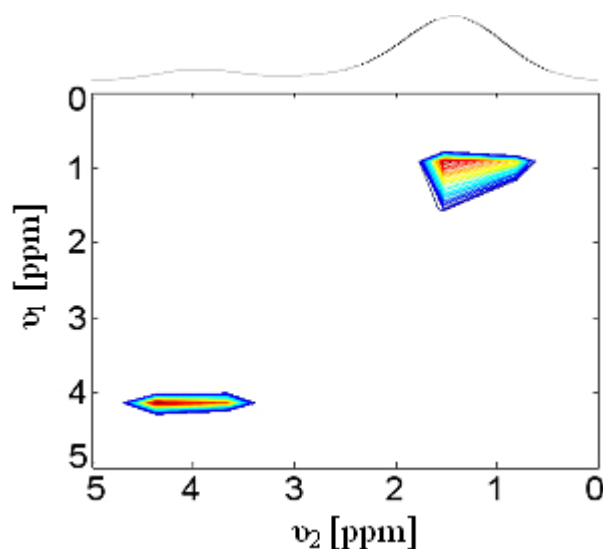


Fig. 6.9 The static ultrafast 2D ^1H NOESY NMR spectrum of a natural rubber sample using the following parameters $G_e = 13$ G/cm, $\Delta O = O_i - O_f = 60$ kHz, 5 ms chirp pulses at a power attenuation of 10 dB, $G_a = 32$ G/cm, $N_2 = 64$, $T_a = 280$ μs (230 μs gradient + 50 μs gradient switching time), 2 μs dwell time, 300 μs purge gradient of 6.5 G/cm, 6 μs 90° hard pulse and 13 μs 180 hard pulse at 6 dB power attenuation. The mixing time was chosen to be $\tau_{\text{mix}} = 0$ in this case. Total experimental time was 0.4s.

The static ultrafast 2D ^1H NOESY NMR spectrum recorded on a natural rubber sample with the cross-link density of 1 phr is shown in Fig. 6.9. The same scheme (Fig. 6.1) previously used for the n-butylchloride liquid sample was applied also in this case. It can be seen that even without any sample rotation, at 500 MHz the CH peak (to the left in Fig. 6.9) is well separated from CH_2 and CH_3 resonances (to the right in Fig. 6.9). The CH_2 and CH_3 resonances are not resolved under static conditions though. Anyway, the ultrafast spectrum in Fig. 6.9 reproduces well the features that should appear in a conventional 2D NOESY spectrum, proving again that the single-scan method is working properly and our solid-state

MAS probe enhanced with a gradient coil along the rotor axis works well under static conditions.

Implementing ultrafast 2D NMR schemes under rotor synchronized MAS conditions should not present a significant challenge, provided that the gradient's $\hat{g}$ orientation is aligned along the rotor axis. Sample spinning effects can then be decoupled from gradient manipulations [Cor1, Dem1] rendering an experiment that, at least from the standpoint of the ultrafast encoding and decoding processes, approaches static-like conditions. Based on such assumption, the gradient-equipped MAS probehead used to record the static natural rubber spectrum in Fig. 6.9 was employed to execute a similar 2D NOESY-type acquisition under sample spinning conditions. Figure 6.10a illustrates the results obtained upon employing this setup to carry out a MAS NMR experiment on the same natural rubber sample.

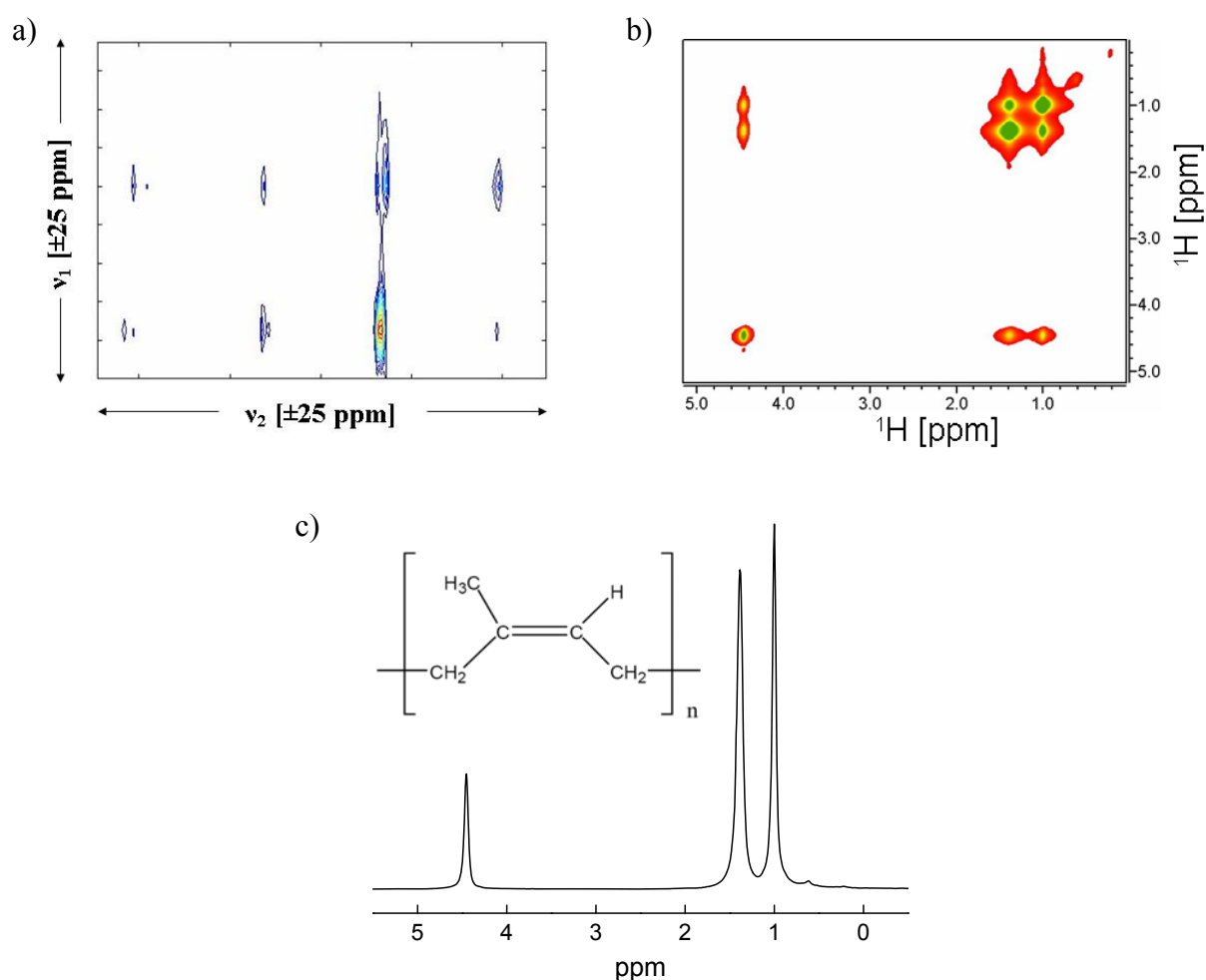


Fig. 6.10 a) Single-scan ^1H 2D cross-relaxation NMR spectra of natural rubber recorded on the same equipment as used to collect the data in Fig. 6.9, but this time subject to 10 kHz MAS rate. Experimental conditions were akin to those employed in that earlier run, except for the spinning and for the mixing time ($\tau_{\text{mix}} = 30$ ms). b) 2D NMR spectrum collected under similar spinning and timing conditions on the same rubber sample, using a conventional acquisition mode. Shown for completion in c) is the analyzed polymer and its single-pulse high-resolution ^1H NMR spectrum at 10 kHz MAS.

Even if repeated over a wide variety of spinning rates and/or gradient strengths, the resulting single-scan 2D experiments yielded few of the easily recognizable spectral features arising when executing 2D cross-relaxation NMR on the same platform with a conventional time-domain protocol (Fig. 6.10b). The reasons underlying this discrepancy between expectation and reality could be many, yet the good results observed under non-spinning conditions suggest discarding those related to poor performances of the RF or to typical gradient setup faults such as eddy currents or slow rise/fall times. This in turn points towards complications associated to the act of mechanical spinning itself, including potential interferences between the various time-dependencies that are present in this experiment.

In order to obtain a better idea on how such factors could interfere with a typical ultrafast 2D acquisition, numerical simulations were carried out capable of solving relaxation-free time-dependent Bloch equations:

$$\begin{aligned}\frac{\partial}{\partial t}M_x(t, \vec{r}) &= -[\Omega_1 + \gamma G_0(t)\hat{g} \cdot \vec{r}(t)]M_y(t, \vec{r}) + \gamma B_1(t)\sin[\varphi_{RF}(t)]M_z(t, \vec{r}) \\ \frac{\partial}{\partial t}M_y(t, \vec{r}) &= [\Omega_1 + \gamma G_0(t)\hat{g} \cdot \vec{r}(t)]M_x(t, \vec{r}) - \gamma B_1(t)\cos[\varphi_{RF}(t)]M_z(t, \vec{r}) \\ \frac{\partial}{\partial t}M_z(t, \vec{r}) &= -\gamma B_1(t)\sin[\varphi_{RF}(t)]M_x(t, \vec{r}) + \gamma B_1(t)\cos[\varphi_{RF}(t)]M_y(t, \vec{r})\end{aligned}\quad (6.5)$$

Notice that within this setting not only the spins' positions $\vec{r}$ but also the gradient's amplitude G_0 as well as the RF's amplitudes γB_1 and phases (i.e., frequencies) Φ_{RF} are allowed to be time-dependent, so as to accommodate the potential effects that sample rotation, gradient oscillations and sweeping offsets could have in the single-scan 2D MAS NMR acquisition. A time propagation of these equations and integration of their resulting transverse complex magnetizations over all possible positions throughout a cylindrical rotor volume

$$S(t) \approx \int_V [M_x(t, \vec{r}) + iM_y(t, \vec{r})] d\vec{r} \quad (6.6)$$

should then mimic the expected experimental signal behavior. This is in fact the same approach as normally used in the simulation of conventional liquid-state ultrafast NMR experiments, except for the fact that in those cases $\hat{g} \equiv \hat{z}$ and $\vec{r}(t)$ simply needs to consider a set of time-independent z coordinates through a sample length L .

With this numerical tool available and with the possibility to experimentally adjust the relative orientation between $\hat{g}$ and the axis of MAS rotation, we set out to explore what new effects could then arise during the implementation of ultrafast 2D acquisitions. Both experiments and simulations confirmed that an exact alignment of $\hat{g}$ along the axis of sample spinning and rapid enough spinning rates, do indeed enable the acquisition of ultrafast 2D

MAS NMR data showing usual features. Fig. 6.11 illustrates this with a series of exchange-type 2D contour plots, collected on a sample of natural rubber using a sequence analogous to that employed in Fig. 6.10 but with the field gradient accurately oriented along the $(\theta_{\text{rot}}, \phi_{\text{rot}})$ direction as described in Experimental Methods. Although the data quality that can be inferred from these results is somewhat lower than that in conventional 2D cross-relaxation experiments, they certainly show several of the features that could be expected from this kind of experiments. Fig. 6.11a for instance exemplifies how, only at high enough spinning rates, will the 2D traces display sharp ^1H centerbands devoid from spinning sidebands – which will otherwise fold over due to the large filter bandwidths which the single-scan 2D NMR experiment needs to operate with. Figure 6.11b in turn shows the build-up of cross-peaks and subsequent fall of both inter- and intra-site resonances, when viewed as a function of the rotor-synchronized cross-relaxation mixing time. Also evident is an asymmetry in the intensities of off-diagonal cross-peaks, which though expected is more marked than in the conventional Fig. 6.10b counterpart.

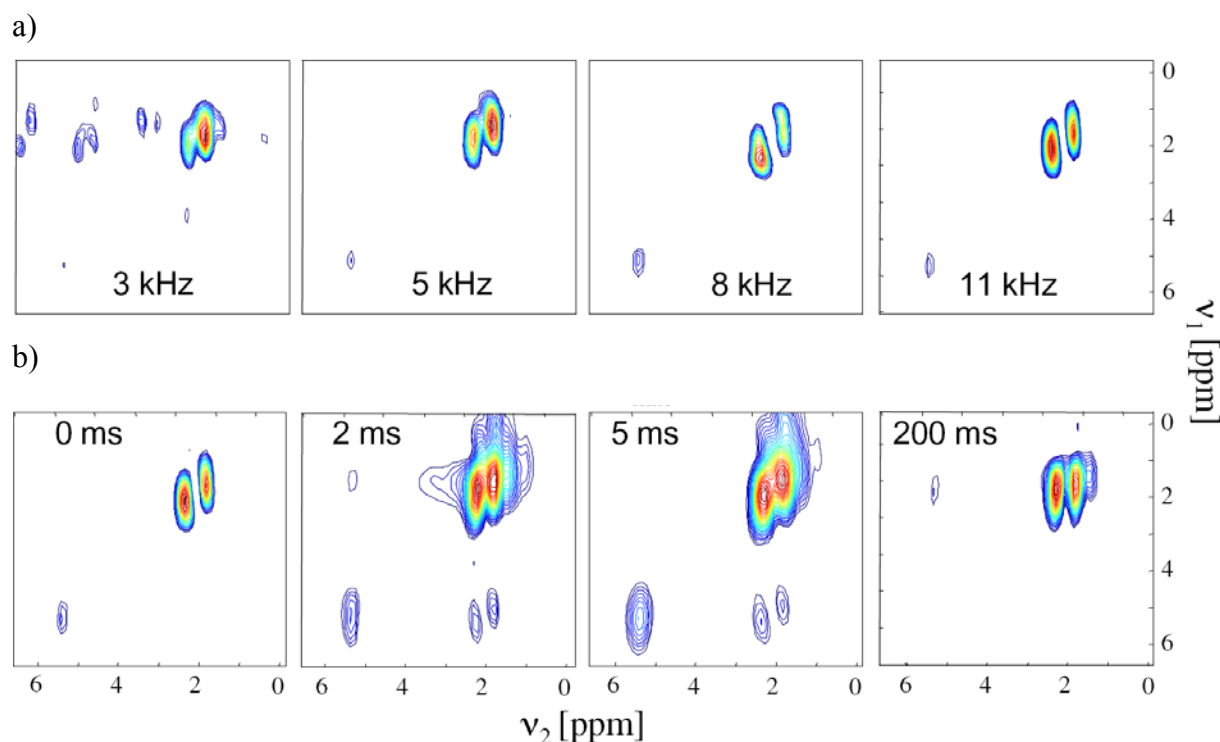


Fig. 6.11 Series of single-scan 2D ^1H exchange NMR spectra collected on natural rubber at a) different spinning rates (with $\tau_{\text{mix}} = 0$) and b) mixing times (at 15 kHz MAS), using a microimaging setup where the effective gradient orientation has been adjusted to coincide with $(\theta_{\text{rot}}, \phi_{\text{rot}})$. Acquisitions parameters: $G_e = 33$ G/cm, RF pulses sweeping over 130 kHz during $t_1^{\text{max}} / 2 = 7$ ms, $G_a = 30$ G/cm, $T_a = 240$ μs , $N_2 = 32$ and zero-filling of the final data to a full 128 x 64 matrix size.

Although both simulations and experiments suggest that reliable single-scan 2D NOESY MAS data can be obtained under optimized circumstances, both approaches point to towards significant spectral non-idealities when small misalignments Δ between the gradient's and the MAS axes orientations arise. Indeed under such conditions, the gradient-derived phase ϕ_G accumulated by spins positioned at spherical coordinates $\vec{r} = (\rho, \beta, \alpha)$ within the rotating sample, will reflect two contributions of differing nature (Fig. 6.12a): a rotationally-invariant one arising from the projection of $\hat{g}$ onto the axis of rotation, and a time-dependent one associated to the transverse component of $\hat{g}$:

$$\begin{aligned}\phi_G(\alpha, \beta, \rho, t) &= \gamma \int_0^t dt' \vec{G}(t') \cdot \vec{r}(t') = \gamma \rho \int_0^t dt' G_0(t') [gr_{\parallel} + gr_{\perp}(t')] \\ &= \gamma \rho \int_0^t dt' G_0(t') [\cos \Delta \cos \beta + \sin \Delta \sin \beta \cos(\alpha + 2\pi \nu_{\text{rot}} t')] \end{aligned} \quad (6.7)$$

where ν_{rot} denotes the MAS spinning rate. Because of their spectroscopic nature, ultrafast NMR experiments design $G_0(t)$ so as to average out the net effects of the gradients, oscillating G_0 to make $\Phi_G(t_1^{\text{max}}) \approx 0$ at the conclusion of the indirect-domain evolution and $\Phi_G(t_2) \approx 0$ within each sampling direct-domain dwell time. 2D MAS NMR experiments operating under the ideal $\Delta = 0$ condition meet these demands, regardless of the spin's position. Upon misaligning the gradient away from the MAS axis, however, a new $gr_{\perp}(t)$ time-dependence arises, capable of interfering with this original balancing out of the gradients. Each (ρ, β, α) position will then experience its own set of non-zero ϕ_G phases, leading to a rapid irreversible decay when considering signals $S(t) = \int_V I(\Omega_1, \Omega_2) \exp[i\phi_G(t, \vec{r})] d\vec{r}$ arising from a full sample volume.

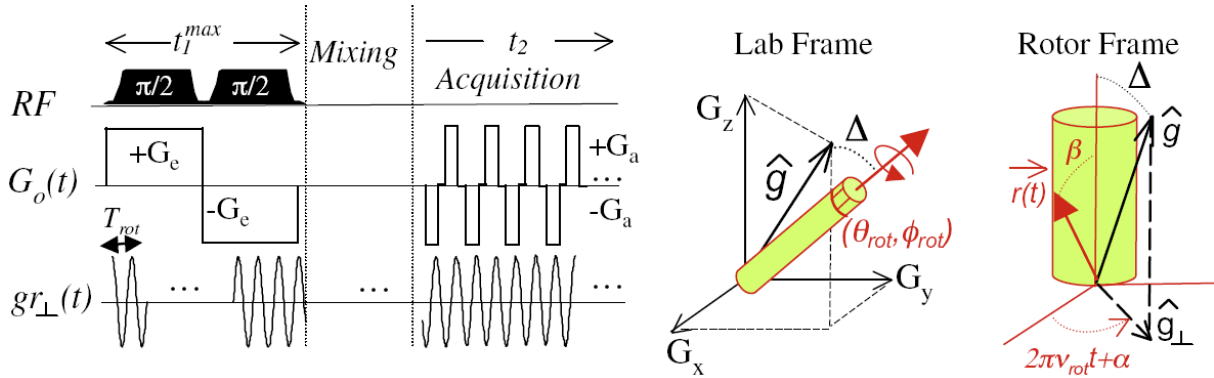
It follows from these arguments that two main processes may be susceptible to the onset of gradient/MAS interferences. One of these will make $\phi_G \neq 0$ at the completion of the indirect-domain spatial encoding; the other will do the same during the progress of the t_2 signal acquisition. If relying on bipolar $\pm G_e$ modulations of the kind employed in Figs. 6.7 or 6.10, the first of these effects will be minor, and experimental efforts to detect them were in fact inconclusive. By contrast, both experiments and numerical simulations point towards the presence of potentially strong ϕ_G interferences arising during the course of t_2 upon making $\Delta = 0$. The strength of these effects can be understood from the very similar time-scales involved in the MAS, given by a rotor period T_{rot} in the order of 100 μs , and by $G_0(t)$ oscillations given by periods Δt_2 of similar duration. Considering for concreteness a square-wave decoding gradient oscillation of basic frequency $(2T_a)^{-1}$

$$G_0(t) = G_a \cdot \text{sgn}\left[2\pi \frac{t}{2T_a}\right] = \frac{4G_a}{\pi} \sum_{n=1,3,5,\dots}^{\infty} \frac{\sin\left(n\pi \frac{t}{T_a}\right)}{n} \quad (6.8)$$

it follows from Eq. (6.7) that destructive interferences are expected whenever the spinning rate $\nu_{\text{rot}} \approx \left(\frac{n}{2T_a}\right)_{n=1,3,5,\dots}$. Fig. 6.12b evidences this effect, with calculations showing the

normalized integrated intensity expected from the $S(t)$ signal for a realistic $2T_a = 200 \mu\text{s}$ dwell time, as a function of increasing rates of sample rotation and for a range of Δ misalignments.

a)



b)

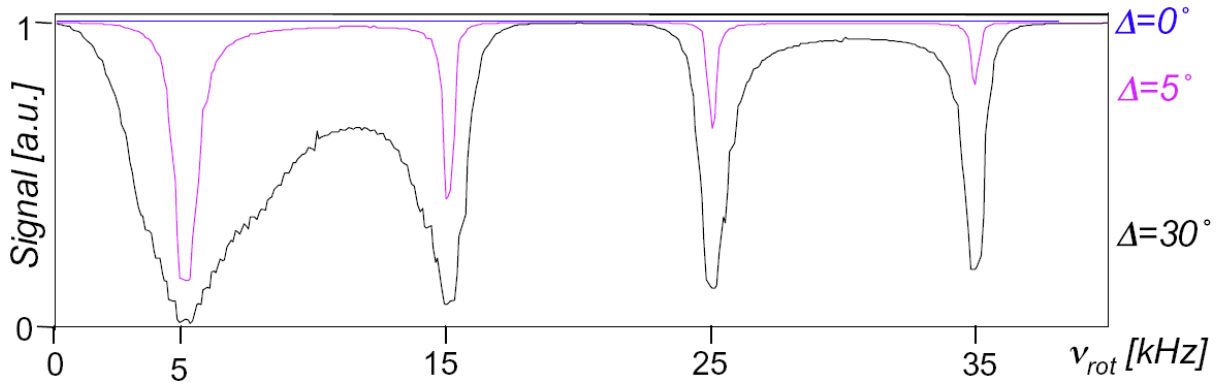


Fig. 6.12 a) New time-dependencies and different angle definitions arising upon having a misalignment Δ between the field gradient employed to implement spatial encoding/decoding, and the axis of MAS. b) Simulated data showing gradient-rotor interference effects during t_2 for a set of fixed decoding parameters ($T_a = 100 \mu\text{s}$, $G_a = 20 \text{ G/cm}$, $N_2 = 16$) calculated as a function of the MAS spinning rate ν_{rot} for different Δ 's. Plotted in the graphs is the overall integral of the signal magnitude $\int_{t_2} |S(t)| dt$, yielding a description of the periodic destructive interference effects as a function of spinning frequency.

Notice the periodicity of the signal attenuation, as well as the decreasing (even if still strong) nature of this effect as the order n of the interfering harmonic increases or as the misalignment

decreases. It follows from this kind of analyses that even small ($\leq 3^\circ$) misalignments can bring about unacceptable signal losses and concomitant peak distortions when operating near

the $\nu_{\text{rot}} \approx \left(\frac{n}{2T_a} \right)_{n=1,3,5\dots}$ resonant conditions; while Δ values exceeding $\approx 20^\circ$ bring about

spectral distortions over a much wider, continuous range of speeds extending all the way up to the maximal spinning rates currently used in this kind of experiments. In a second manifestation of these interferences, Fig. 6.13 illustrates experimental time-domain signals collected for fixed $\Delta = 30^\circ$ and $\nu_{\text{rot}} = 5$ kHz values as a function of changing T_a gradient oscillation times, for both a liquid and a solid sample. Owing to its longer T_2 transverse relaxation decay the former sample evidences more clearly the above-mentioned interference;

in both instances, however, the fast decay trend for the $T_a \approx \left(\frac{n}{2\nu_{\text{rot}}} \right)_{n=1,3,5\dots}$ condition is apparent.

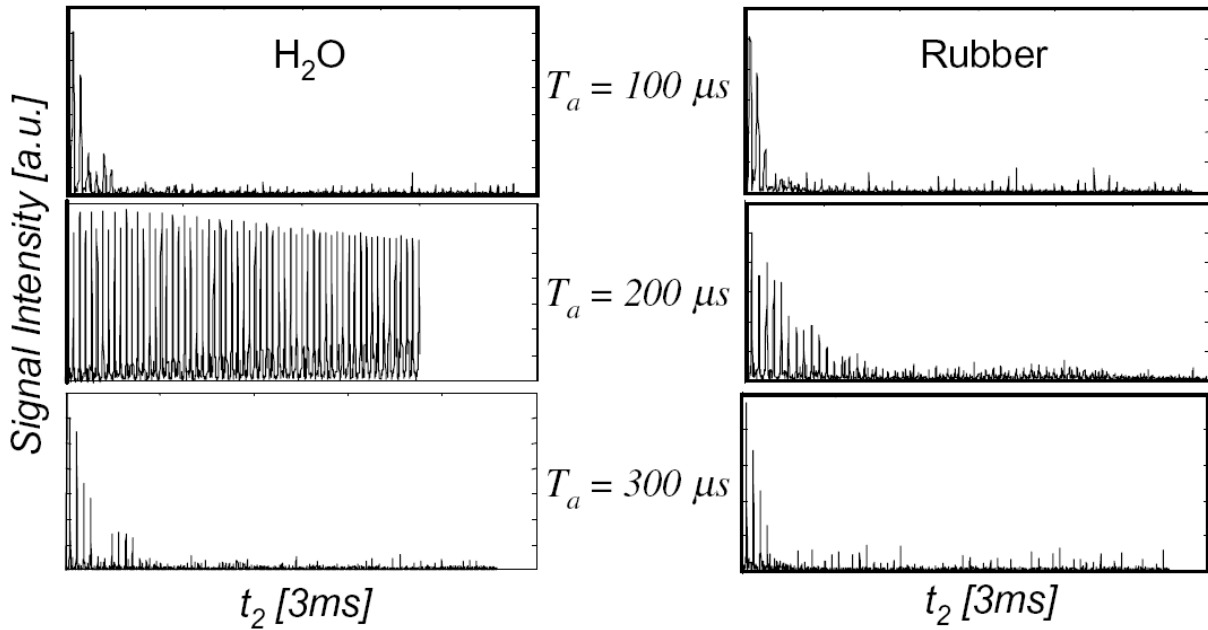


Fig. 6.13 Experimental examples of the t_2 interference effects on water (left) and rubber (right) samples, when an off-angle of 30° is inserted between the gradient- and the rotor-axes during acquisition. The spinning speed was now kept constant at 5 kHz, and the indicated T_a durations were changed. The sequence used is as in Fig. 6.1 with $G_e = 30$ G/cm, $G_a = 33$ G/cm, RF chirp duration = 3 ms, $N_2 = 64$.

6.4 Hyperpolarized ^{129}Xe 2D NMR spectroscopy of porous polymers

Porous polymers have many applications as oxygenating membranes, drug delivery systems or proton-exchange membranes used for fuel cells. Characterization of pore networks is an important topic in materials research. Nuclear magnetic resonance offers unique opportunities in this area, by exploiting the exchange of molecules penetrating the pore network. Such molecules can be represented by water, organic solvents, SF_6 and, in our case, thermally polarized or hyperpolarized ^{129}Xe . The NMR experiments that reveal the exchange between different sites in the investigated system are 2D *EXchange SpectroscopY* (EXSY) (Fig. 6.2) and 2D experiments based on the inverse Laplace transform.

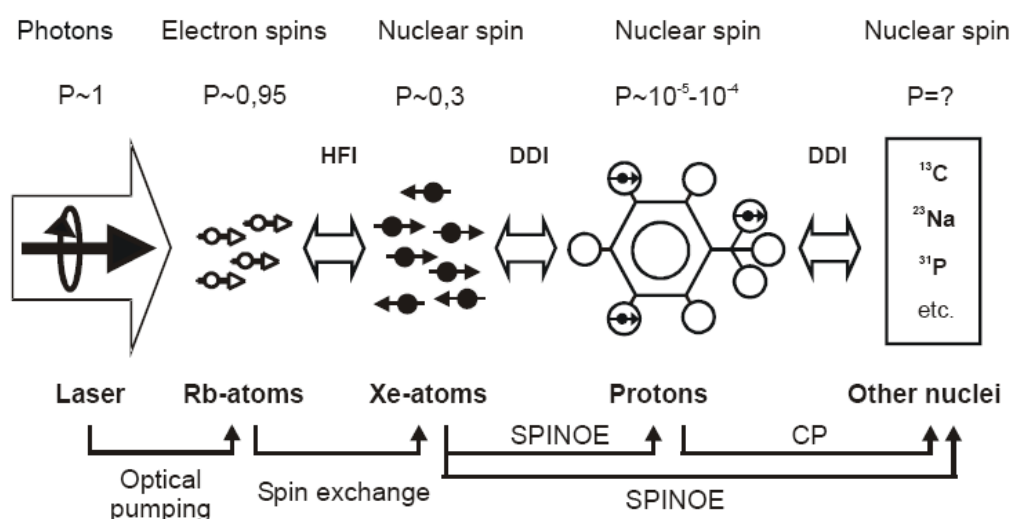
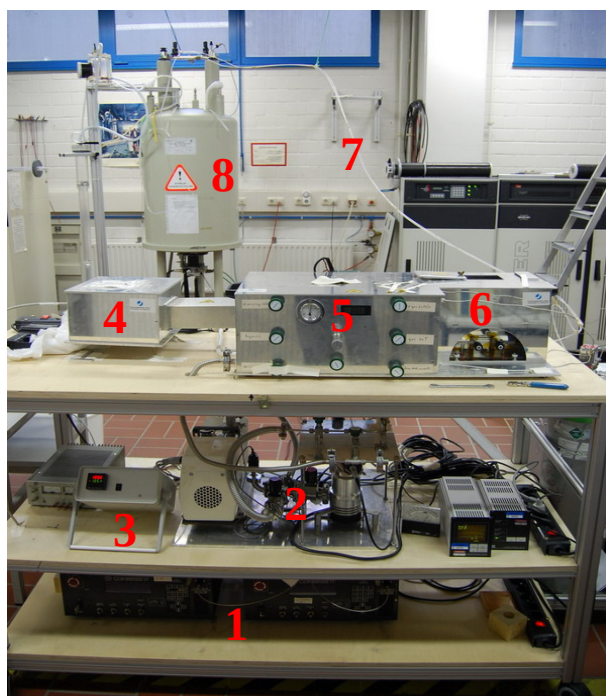


Fig. 6.14 Principle of spin-exchange optical pumping: polarization is transferred from photons to Rb-atoms by optical pumping, from the electron spin to the nuclear spin of Xe by hyperfine interaction (HFI) and from the Xe spins to other nuclear spins by dipole-dipole interaction (DDI). The magnitudes of the spin polarization P for each step are indicated at the top of the figure [App1].

The hyperpolarization process makes use of *spin-exchange optical pumping*, which is the notation of a mechanism for the transfer of angular momentum from circular polarized laser light to electronic and afterwards to nuclear spins [Hap1, Wal1, App2]. It is capable of producing moderate to high levels of nuclear spin polarization in xenon and helium under a wide range of conditions (e. g. temperature, gas pressure, and field strength). The first step of this mechanism, the optical pumping, was discovered by Kastler in 1950 [Kas1], for which he

was awarded the Nobel Prize in Physics in 1966. The second step, the ability to transfer polarization from electron to nuclear spins, was found by Bouchiat et al. in 1961 [Bou1]. Under optimized conditions laser-polarized xenon can give sensitivity enhancement of as much as 10^5 compared to thermally polarized xenon [Gae1]. Figure 6.14 represents a schematic overview of the hyperpolarization process. The absorption of the circular polarized laser light by the Rb-atoms leads to a nearly perfect polarization of the Rb electron spins. The ordered Rb electron spins experience many interactions with each other and the gases (helium, nitrogen and xenon) which are present in the optical pumping cell. During a collision with other Rb atoms they undergo a flip-flop process, which does not lead to a loss of polarization. Collisions with Xe-atoms cause the exchange of polarization by hyperfine coupling of the Rb electron spin to the nuclear spin of Xe. If the Xe atoms get in contact with different nuclei (for example the protons of toluene like in Fig. 6.14) they can transfer their polarization via SPINOE (Spin Polarization Induced Nuclear Overhauser Effect) [Nav1, Son1, Son2, App3, Cav1]. The SPINOE is driven by dipole-dipole interactions and therefore works best if the distance between the Xe and the interacting atom is small and the correlation time is long. For that reason, the most efficient polarization transfer takes place between Xe and protons, which results in a high net magnetization of protons which can exchange their polarization by cross polarization (CP) with other nuclei.

a)



1. 30W lasers
2. vacuum pump
3. temperature controller
4. lasers combiner
5. flowmeter
6. pumping cell
7. plastic tube
8. 200 MHz NMR spectrometer

b)

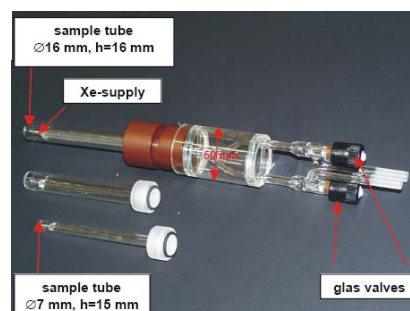


Fig. 6.15 a) Rb-Xe hyperpolarizer located in the Magnetic Resonance Center of RWTH Aachen University. It was developed and constructed by S. Appelt and coworkers in the research center Jülich. b) Probe for measurements with hyperpolarized Xe. It consists of an inflow and an outflow part.

The hyperpolarizer used in this work was built at the Research Center Jülich by the group of S. Appelt. It is shown in Fig. 6.15. The gas mixture used for hyperpolarization consists of 98% helium, 1% nitrogen and 1% xenon (natural abundance of ^{129}Xe) at a pressure of 7 bar. The gas flow through the pumping cell and the whole apparatus can be regulated by a needle valve and controlled by a flowmeter. The typical flow rate used was about 300 cm^3/min . The pumping cell which consists of a borosilicate glass cylinder (inner diameter: 2.4 cm, length: 7 cm) and the Rb reservoir (1 g Rb applied on a copper mesh) are surrounded by a hot air oven in order to evaporate the Rb to the gas phase. The temperature for optical pumping used in this work varied in the range of 160-180° C. The Rb vapor is transported by the ^4He , N_2 , Xe gas stream inside the optical pumping cell which is exposed to a laser beam of circular polarized light with a wave length of 795 nm. The optical pumping cell is centered in a pair of Helmholtz coils that produce a homogeneous magnetic field of 70.7 G, which is necessary for the optical pumping process. During the time the Xe atoms need to pass the optical pumping cell (depending on the gas flow rate between a few seconds and half a minute) they get hyperpolarized by spin-exchange optical pumping. Used in continuous flow mode, the hyperpolarized Xe flows through a 7 meter plastic tube directly into the sample cell which is positioned in a 200 MHz spectrometer. The total degree of polarization which was achieved by this hyperpolarizer varied in the range of 20% to 35 % depending on the experimental conditions [App1].

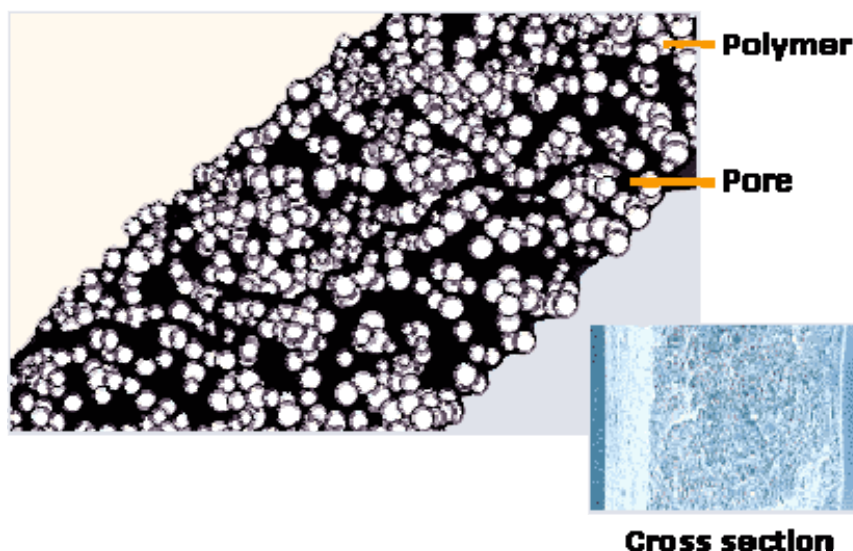


Fig. 6.16 Schematic representation of a porous polymer and the SEM cross-section of polypropylene membrane (OXYPHAN®) used for blood oxygenation.

In this study, the ^{129}Xe NMR experiments were performed on an OXYPHAN® polypropylene (PP) membrane produced by MEMBRANA GmbH. This sponge-like material

has very high porosity with uniform pore distribution and excellent gas permeability (Fig. 6.16), being the membrane of choice in oxygenation due to its renowned performance and ease of handling and processing. The maximum pore size given by MEMBRANA is 0.2 μm .

A standard hyperpolarized ^{129}Xe spectrum of this porous polypropylene membrane measured in one scan is shown in Fig. 6.17. Besides the intense ^{129}Xe free gas signal, defining the origin of the spectrum, two other weaker signals are detected around 35 ppm and 225 ppm. The first is assigned to ^{129}Xe atoms in the pores of PP, and the other one to the ^{129}Xe atoms in the free volume of PP.

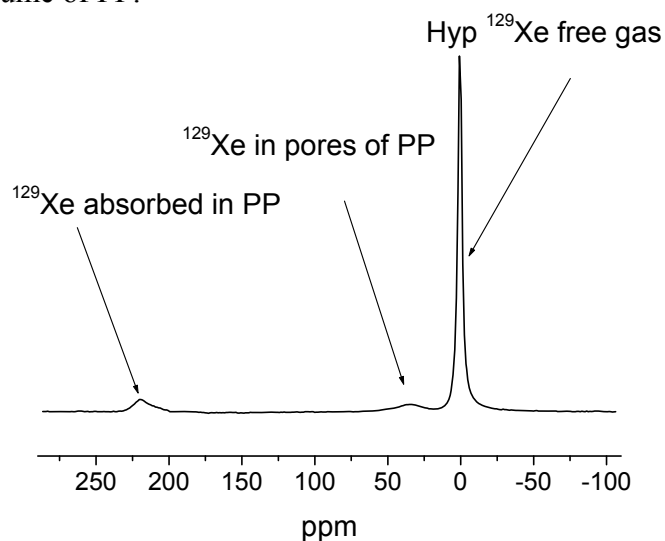


Fig. 6.17 One-scan hyperpolarized ^{129}Xe NMR spectrum of OXYPHAN[®] polypropylene membrane.

In order to quantitatively characterize the exchange process between the free Xe gas and the Xe absorbed in the polymer material, two different methods have been used. The first one is based on a selective inversion of the signal corresponding to the Xe atoms penetrating the PP matrix, as depicted in Fig. 6.18.

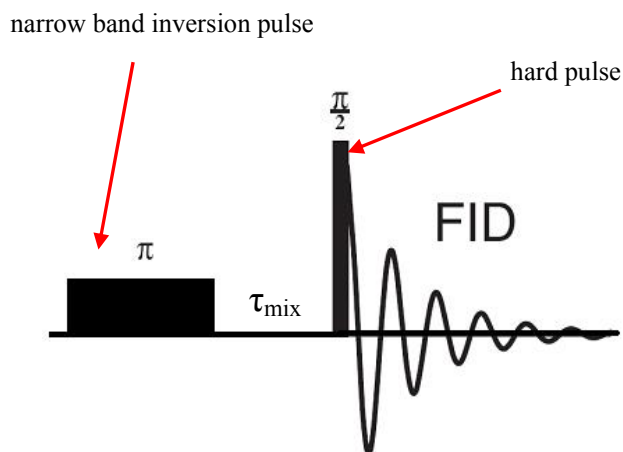


Fig. 6.18 Pulse scheme used for the experiment of selective inversion recovery of the signal corresponding to the Xe absorbed in the OXYPHAN[®] PP membrane.

By systematically increasing the τ_{mix} delay between the 90° soft pulse (at the resonance frequency of the Xe atoms absorbed in PP) and the 90° hard pulse (see Fig. 6.18), the evolution of the intensity of the 225 ppm signal was evaluated. A series of 1D hyperpolarized ^{129}Xe spectra was recorded as a function of τ_{mix} (Fig. 6.19a) and the integral of the signal at 225 ppm was measured and plotted against τ_{mix} (Fig. 6.19b). Extrapolating the value corresponding to 0 peak intensity in Fig. 6.19b, the Xe exchange rate could be estimated. The value found is about 800 μs , demonstrating a very fast exchange of the Xe atoms between the free gas and the polymer free volume.

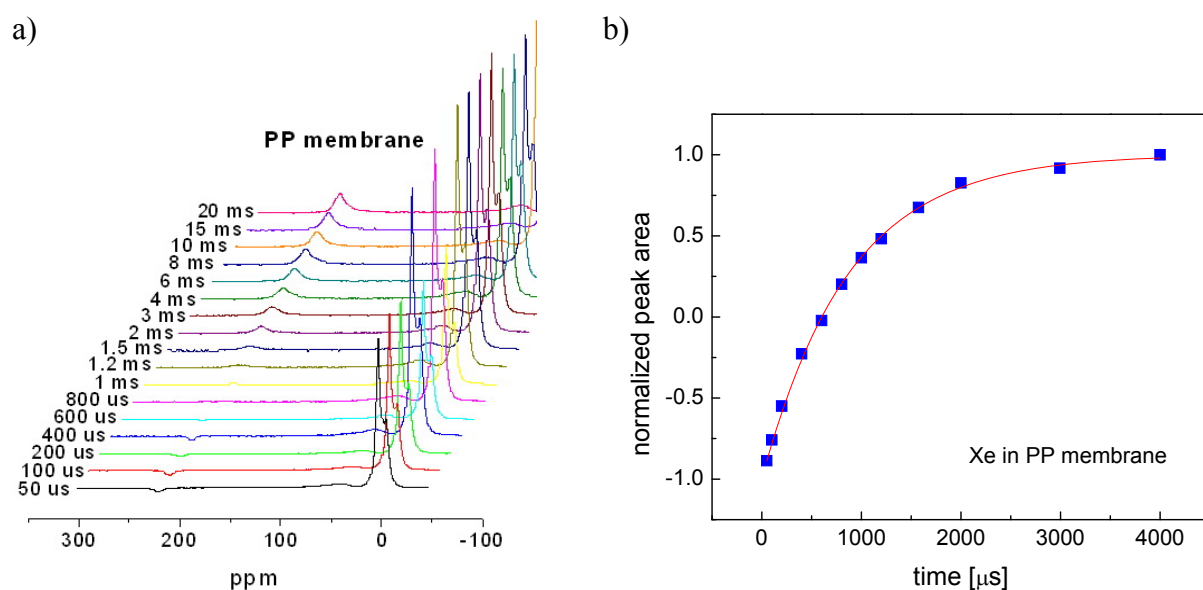


Fig. 6.19 a) Series of 1D hyperpolarized ^{129}Xe spectra obtained using the pulse scheme from Fig. 6.18 as a function of the mixing time τ_{mix} . b) Relative integral of the signal at 225 ppm as a function of τ_{mix} .

The exchange of Xe atoms is expected to take place between all three pools: free gas, polymer free volume and polymer pores. In order to test this assumption, 2D EXSY (Fig. 6.2) was performed on the OXYPHAN[®] membrane. The obtained 2D spectrum using a $\tau_{\text{mix}} = 50$ ms mixing time is shown in Fig. 6.20, with the presence of the three diagonal peaks corresponding to the three different sites in which the Xe atoms can be found, and the well defined cross-peaks proving the exchange between all these different sites. Due to a reduced number of pores, so a reduced total volume of pores compared to the free volume in the PP membrane, the diagonal signal of Xe in the pores has very low intensity.

The exchange rates of the Xe atoms can be quantitatively studied with a series of 2D EXSY spectra acquired with different mixing times τ_{mix} . The dependence of the integral area of 2D peaks (diagonal and off-diagonal) is shown in Fig. 6.21. It is evident that at least in the initial regime the rate of exchange between the free gas and the Xe in the free volume of the polymer is equal to the rate of exchange for the reverse process.

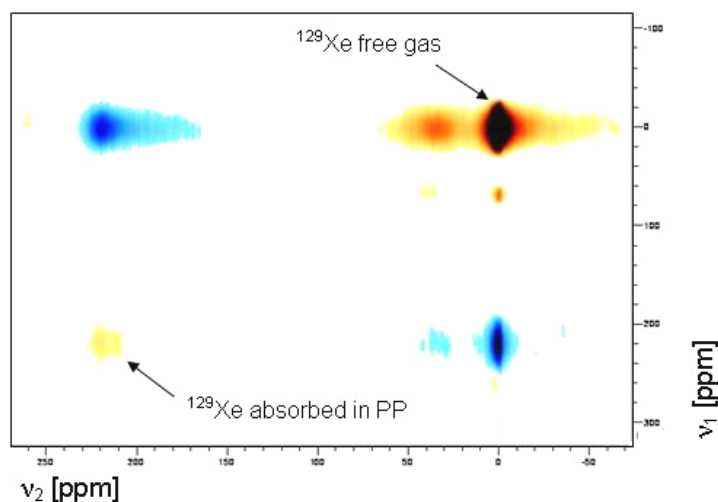


Fig. 6.20 Two-dimensional EXSY spectrum of hyperpolarized ^{129}Xe in the porous PP membrane. The total duration of the experiment was 42 minutes and the mixing time $\tau_{\text{mix}} = 50$ ms.

This preliminary study reveals the possibility of using multidimensional NMR experiments together with the hyperpolarized ^{129}Xe for investigating the morphology of porous polymers. The high signal-to-noise ratio offered by hyperpolarized ^{129}Xe gives access, in reasonable time, to quantitative information using 2D NMR spectroscopy.

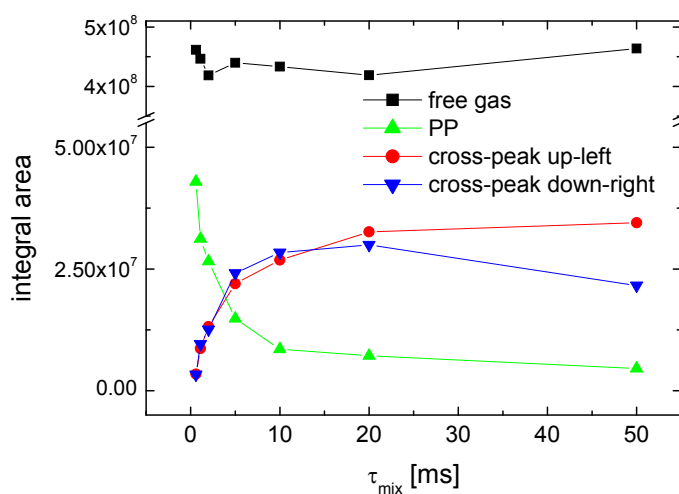


Fig. 6.21 The dependence of the integral area of diagonal and off-diagonal peaks in 2D EXSY spectra as a function of the mixing time.

6.5 Conclusions

The combination of gradient-based single-scan 2D NMR procedures with MAS could yield significant benefits, and is a simple procedure provided that the spectrometer delivers the required performance. As shown by this study such requirements can be met by existing pulse

sequences, if commercial MAS and microimaging setups are combined and their relevant axes are precisely co-aligned. Given these facts, one could conceive furthering the kind of work hereby presented in two complementary research directions. One involves a spectroscopic route, whereby different alternatives are explored so as to alleviate the stringent demands imposed by MAS on the gradient alignment. In this respect it is likely that constant-gradient t_2 decoding approaches of the kind that have been recently demonstrated [Shr2], could be more immune to Δ gradient deviations than their oscillating-gradient counterparts. Another, more applied direction, concerns exploiting the kind of measurements that were successfully illustrated in this study, to explore by NMR solid systems that are not amenable to lengthy conventional 2D acquisitions. Given the signal-to-noise limitations of single-scan 2D experiments we envision that such studies will mostly entail ^1H observations. Given MAS limitations to deliver high-resolution in such instances, studies on soft- or semi-solids like the one analyzed in this work appear as most likely targets. Even under such constraints several applications can be conceived, involving for example studies on unstable samples, dynamic experiments monitoring the return of chemical systems back to equilibrium, or measurements on hyperpolarized samples.

Ultrafast multidimensional NMR spectroscopy can be combined with the technique of laser hyperpolarized ^{129}Xe for the investigation of porous materials and biopolymers. In this work the possibility of using hyperpolarized ^{129}Xe for performing 2D EXSY experiments on a porous polymer membrane has been demonstrated. The combination of this method with the ultrafast multidimensional spectroscopy is a topic for the future.

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7 Morphology and side-chain dynamics in hydrated hard α -keratin fibres by ^1H solid-state NMR

7.1 Introduction

The importance of the hydration water for protein folding was realized after introducing the concept of *hydrophobicity* related to protein stability [Kau1]. Therefore, a *protein* should have been defined as a system *peptide+water* [Fra1, Zha1] since the simple biomolecule is not able to perform its biological activity without at least one layer of water surrounding it. The protein functionality is related to conformational flexibility that is directly connected to its hydrogen bonds with hydration water.

The hard α -keratin is a filamentous protein found in mammalian epidermal appendages (hairs, horn, nails, etc.) distinct from feather β -keratin found in avian and reptilian tissues. As a component of skin, hair and nail tissues act as an interface between the living organisms and the external environment. Recently, a ^{13}C and ^2H solid-state NMR study of an α -keratin sourced from equine hoof has revealed a strong dependence of molecular conformation and molecular dynamics on the degree of hydration of the material [Due1]. In particular, dehydration results in a much more ordered structure, with a loss of α -helical components in the structure and partial breaking of cysteine disulfide bonds. Moreover, the morphology and molecular mobility changes of the side-chains of hard α -keratin following the thermal denaturation or induced by oxidative and reductive-oxidative treatments were investigated by ^1H , ^{13}C and ^{129}Xe NMR spectroscopy and ^1H spin-diffusion [Mel1]. A qualitative model describing the changes induced in hard α -keratin protein by these processes was developed and showed to correlate with the changes in domain thickness, phase composition and molecular dynamics.

The aim of this work is to investigate the morphological and molecular dynamics changes induced by hydration of hard α -keratin. The phase (fraction) composition and side-chain dynamics were measured on Caucasian hair at different levels of hydration by ^1H wide-line spectra. The sizes of rigid and mobile domains were determined by ^1H spin-diffusion

using the initial-rate approximation in combination with the quasi-equilibrium ratio of the NMR signals.

7.2 Experimental

The hard α -keratin fibers used for this study were of Caucasian dark-brown hair, supplied by Kerling International Haarfabrik GmbH, Germany. The fibers were cleaned with 1% lauryl ether sulphate (LES) and dried at room temperature prior to working with them. The pH of their aqueous extract was found to be 6.5 to 7.

For the NMR measurements the samples were cut into fine snippets (about 2 mm). Samples with different moisture contents were prepared by leaving for 12 hours the hair snippets into a home-built chamber with automatic control of temperature and relative humidity (RH). A series of samples with 55%, 65%, 75%, 85% and 100% RH respectively were made at 22° C. After 12 hours of moisture equilibration in the chamber, the snippets were transferred into the measuring NMR rotor and sealed. A dry sample (at 0% RH) was prepared by heating the hair snippets for 24 hours at 100° C under vacuum, transferred into the NMR rotor and sealed.

Proton solid-state NMR spectra and ^1H spin-diffusion were measured on a Bruker Avance III 700 spectrometer. Proton NMR data were collected with the 3.2 mm CPMAS probe at room temperature for non-spinning samples. The dead time of the spectrometer is 5.5 μs . The length of the $\pi/2$ pulse was 2.5 μs , the dwell time was 2 μs and the recycle delay was 3 s for all measurements.

The proton wide-line spectra were decomposed into three or four components using the DMFIT program. The broad component describing the rigid fraction in the spectra was approximated by a Gaussian function. A Lorentzian line shape was used to describe the narrow components of the spectra corresponding to the mobile phase and water. A combination of Gaussian and Lorentzian functions was used to describe the intermediate line corresponding to the interface. The decomposition algorithm is convergent only if a Gauss line-shape is considered for the water fraction.

Proton spin-diffusion measurements were performed using the general scheme consisting of a double-quantum (DQ) dipolar filter, a spin-diffusion period and an acquisition period [Mel1 and references therein]. A gradient of magnetization was created by the dipolar filter that generates DQ coherences and selects mainly the magnetization of the rigid phase

(fraction). The value of the excitation/reconversion times used for the DQ dipolar filter in the spin-diffusion experiments was $\tau = 7 \mu\text{s}$. It corresponds to the rising region of the DQ build-up curve for each sample [Mel1].

7.3 Theory

The transport of z-magnetization oriented along the static magnetic field in an NMR experiment can be described by the diffusion equation in the continuum approximation. The concentration $m(\vec{r}, t)$ of nuclear z-magnetization at the position $\vec{r}$ in the sample relative to the centre of symmetry of different morphologies at the moment of time t is defined by

$$m(\vec{r}, t) = \frac{M_z(\vec{r}, t)}{\rho(\vec{r})\Delta V(\vec{r})}, \quad (7.1)$$

where $M_z(\vec{r}, t)$ is the total z-magnetization and $\Delta V(\vec{r})$ is the infinitesimal volume around the point defined by the vector $\vec{r}$. The number density of spins is denoted by $\rho(\vec{r})$.

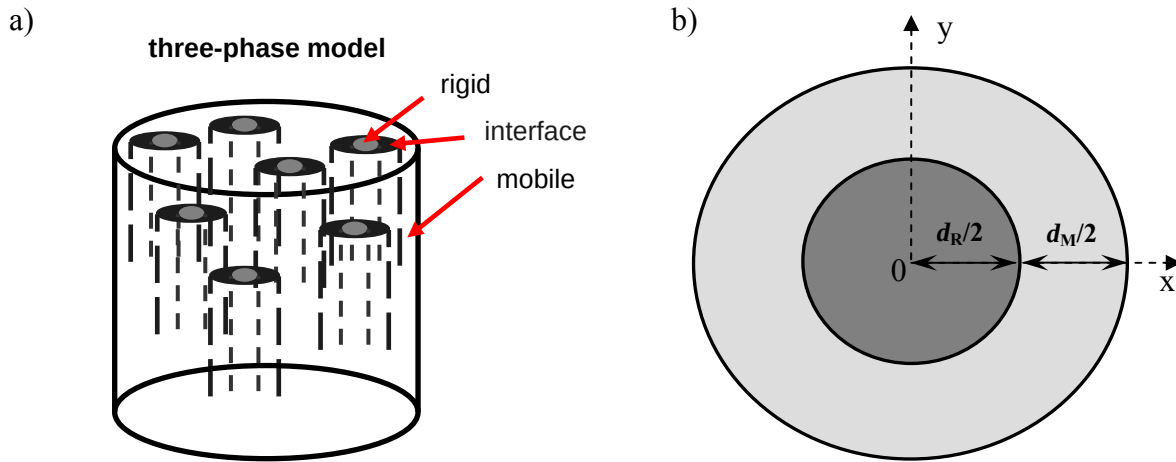


Fig. 7.1 a) Schematic representation of the three-phase model of keratin fibres. The intermediate filaments (IF) are imbedded in an amorphous keratin matrix and stabilized by the interface. b) The cylindrical morphologies with finite source (rigid domain) and finite sink (mobile domain) used to discuss the initial regime of the spin-diffusion process. The diameter of the rigid domain is denoted d_R and the thickness of the surrounding cylindrical layer $d_M/2$.

In the limit of isotropic spin-diffusion and spatially constant spin diffusivity (D) the spin diffusion equation has the form [Sch1, Van1, Dem1]

$$\frac{\partial m(\vec{r}, t)}{\partial t} = D \nabla^2 m(\vec{r}, t). \quad (7.2)$$

The instantaneous NMR observables in a spin-diffusion experiment are represented by the normalized integral intensity $I_i(t)/I_0$ of the i^{th} component of the NMR spectrum with the total integral intensity I_0 . More specifically, the normalized NMR spin-diffusion observables for well defined domain sizes can be expressed as

$$\frac{I_i(t)}{I_0} = \frac{\iiint_{V_i} \rho_i m_i(\vec{r}, t) d\vec{r}}{I_0}, \quad (7.3)$$

where V_i is the volume of the i^{th} domain.

In many cases we have to consider an ensemble average over a distribution of domain sizes [Dem1]. In the absence of additional information about the system indicating intrinsic organization in phase dimensions we consider that the Gaussian distribution function is appropriate

$$P(d) = \frac{2}{\pi \bar{d}} \exp \left\{ -\frac{1}{\pi} \left(\frac{d}{\bar{d}} \right)^2 \right\}, \quad (7.4)$$

where $\bar{d}$ is the mean linear dimension for the domain. In this case the spin diffusion NMR observable is given by

$$\left\langle \frac{I_i(t)}{I_0} \right\rangle = \int_0^\infty P(d_i) \frac{I_i(t)}{I_0} d(d_i), \quad (7.5)$$

where d_i is d_R and d_M for the rigid and mobile domain sizes, respectively. If the spin-lattice relaxation can be neglected we can write

$$\left\langle \frac{I_R(t)}{I_0} \right\rangle + \left\langle \frac{I_M(t)}{I_0} \right\rangle = 1. \quad (7.6)$$

A simple procedure to obtain domain sizes is that based on the initial rate approximation [Sch2]. We made the following assumptions: (i) the three phases morphology of hard α -keratin (Fig. 7.1a) is approximated by a rigid (R) and a mobile (M) domain; (ii) the source of magnetization is represented by a cylinder with the radius $\bar{d}_R/2$ and the sink is located in the concentric cylinder with the thickness of $\bar{d}_M/2$; (iii) the spin density is $\rho_R \approx \rho_M$ and (iv) the heterogeneous medium is modelled with an effective spin diffusivity $D_{\text{eff}} = c_R D_R + c_M D_M$, where c_R and c_M are the concentrations of the spins in both domains. In the initial rate approximation the spin diffusivity D_M can be approximated by the interfacial value D_I . Since, $D_R > D_I, D_M$ and $c_R > c_M$ (*vide infra*) we can write in a good approximation $D_{\text{eff}} \approx D_R$.

The time evolution of the spin diffusion observable of the magnetization source (R) in the limit of the above approximations is given by [Dem1, Cra1, and references therein]

$$\left\langle \frac{I_R(t)}{I_0} \right\rangle = \frac{E}{1+E} - \sum \frac{8E}{4E^2 + 4E + q_n^2} \cdot \frac{1}{q_n} \frac{J_1(q_n)}{J_0(q_n)} \exp \left\{ -\frac{4}{\sqrt{\pi}} \cdot \frac{q_n \sqrt{D_{eff} t}}{\bar{d}_R} \right\}, \quad (7.7)$$

where $J_n(x)$ is a Bessel function of integer order n , and q_n are the positive, non-zero roots of the equation

$$q_n J_0(q_n) + 2E J_1(q_n) = 0. \quad (7.8)$$

The ratio of the spin-diffusion signals at the end of the process is denoted by $E = \langle I_M^{eq} \rangle / \langle I_R^{eq} \rangle$.

It is easy to show that for the cylindrical morphology we finally get

$$\frac{\bar{d}_M}{\bar{d}_R} = [1 + E]^{1/2} - 1. \quad (7.9)$$

In the initial regime of the spin-diffusion decay curve, i.e., for $\bar{d}_R \gg \sqrt{D_{eff} t}$, the spin-diffusion observable of Eq. (7.7) changes linearly in $\sqrt{t}$. The spin-diffusion decay curve approximately described by Eq. (7.7) has an initial slope a straight line that intersects the $\sqrt{t}$ axis at $\sqrt{t_0}$. Hence, the domain thickness d_R for cylindrical morphology is given by

$$\bar{d}_R = \frac{16}{\sqrt{\pi}} \sqrt{D_{eff} t_0} \sum_{n=1}^{\infty} \frac{q_n}{4E^2 + 4E + q_n^2}. \quad (7.10)$$

So the Eqs. (7.8)-(7.10) give a simple procedure to evaluate the average values of $\bar{d}_R$ and $\bar{d}_R$.

7.4 Results and discussion

7.4.1 Phase composition

In the hydrated hard α -keratin the decomposition of the ^1H wideline NMR spectra was made with four components, corresponding to rigid phase, interface, mobile phase and water (Fig. 7.2). Only the first three components were used for dehydrated keratin sample. The fraction composition is shown in Fig. 7.3a as a function of relative humidity (RH). The increase in the amount of water with increasing RH value follows a sigmoidal curve similar to that measured for moisture uptake [Pop1]. In the dehydrated hard α -keratin, the amount of rigid fraction has a low value as opposed to the hydrated keratin (Fig. 7.3a). This may indicate the formation of

an ordered hydration shell around the proteins of the keratin intermediate filament (KIF) [Yok1]. The mobile fraction decreases monotonically with RH value, probably due to the formation of hydrogen bonds stabilizing the protein-protein interfaces [Iku1] and hindering the motion of the side-chains. The interfacial region has the largest value for the dehydrated sample. Its fraction decreases and seems to level off with increasing RH values.

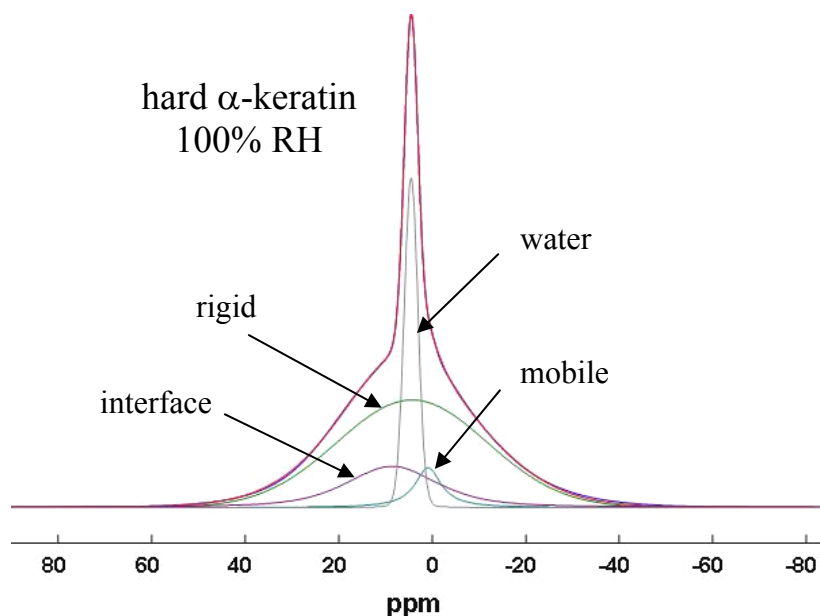


Fig. 7.2 Decomposition into four components of the proton spectrum of Caucasian hair hydrated at 100% RH.

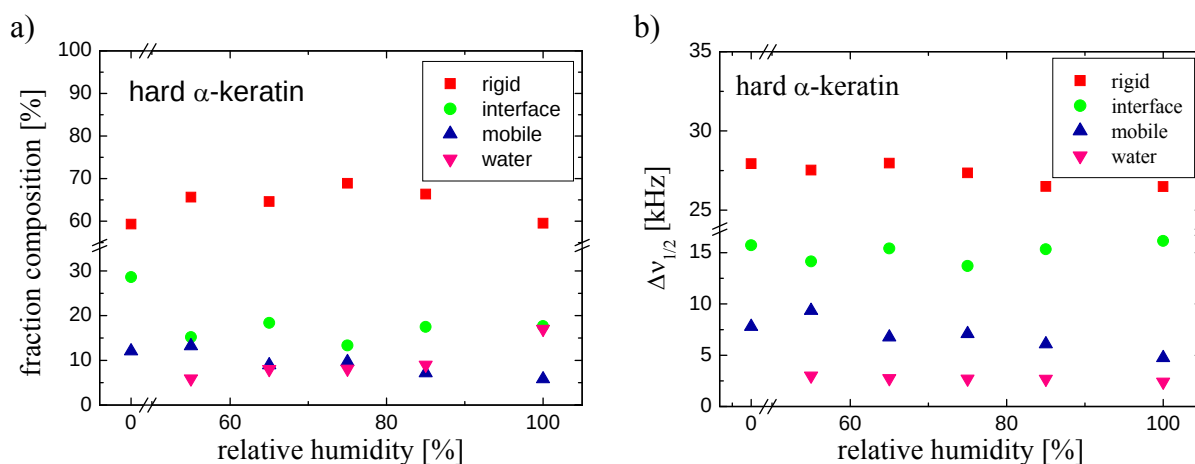


Fig. 7.3 a) Phase composition and b) full linewidth at half height ($\Delta\nu_{1/2}$) of spectral component for hydrated Caucasian hair measured at room temperature as a function of relative humidity.

7.4.2 Side-chain dynamics

The aminoacid side-chain dynamics is reflected in the linewidth at the half height ($\Delta\nu_{1/2}$) of the ^1H NMR spectral components shown in Fig. 7.3b. The decomposition of the ^1H spectra

reveals only the presence of the bound water with $\Delta\nu_{1/2} \approx 2.5$ kHz that remains almost constant at different RH. The rigid fraction has the lowest molecular mobility for the dehydrated sample, and it increases with the hydration level. The same trend is visible in Fig. 7.3b for the mobile fraction. The NMR procedure used for this investigation does not detect any significant changes in the side-chain dynamics of the interfacial region.

7.4.3 Relative domain sizes

In order to evaluate the average domain sizes, spin diffusivity of the rigid domain has to be estimated using the relationship $D_R = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln 2}} \langle r^2 \rangle \Delta\nu_{1/2}$, where $\langle r^2 \rangle$ is the mean square distance between the nearest spins [Dem1]. In order to avoid the estimation of $\langle r^2 \rangle$, which is difficult to evaluate for the keratin α -helix, the normalized values of $\bar{d}_R$ to $\bar{d}_R^{dry}$ have been calculated (where $\bar{d}_R^{dry}$ refers to dry keratin). From Eq. (7.10) one can write

$$\frac{\bar{d}_R}{\bar{d}_R^{dry}} = \sqrt{\frac{\Delta\nu_{1/2} t_0}{\Delta\nu_{1/2}^{dry} t_0^{dry}}} \frac{\sum_{n=1}^{\infty} s_n}{\sum_{n=1}^{\infty} s_n^{dry}}, \quad (7.11)$$

where s_n and s_n^{dry} are the arguments in the sum of Eq. (7.10). The values for the quantities $\Delta\nu_{1/2}$, t_0 and E are given in Table 7.1. The ratio $\bar{d}_M / \bar{d}_M^{dry}$ for the mobile phase is obtained from Eq. (7.9) and Eq. (7.10).

Table 7.1 Full linewidth at half height $\Delta\nu_{1/2}$ of rigid spectral component, spin-diffusion intersection parameter $\sqrt{t_0}$ and integral intensity ratio E as a function of relative hydration (RH) for Caucasian hair.

RH [%]	$\Delta\nu_{1/2}$ [kHz]	$t_0^{1/2}$ [ms ^{1/2}] ^a	E ^b
0	27.9	7.8	0.16
55	27.5	9.4	0.31
65	27.9	9.7	0.38
75	27.4	10.4	0.39
85	26.5	12.0	0.44
100	26.5	11.2	0.81

^aErrors of the order of 10%

^bErrors of the order of 5%

A stack plot of ^1H NMR spectra measured at different spin-diffusion times t is shown in Fig. 7.4a. They were decomposed into two components and their normalized integral intensities are shown in Fig. 7.4b as a function of t for the sample with 100% RH.

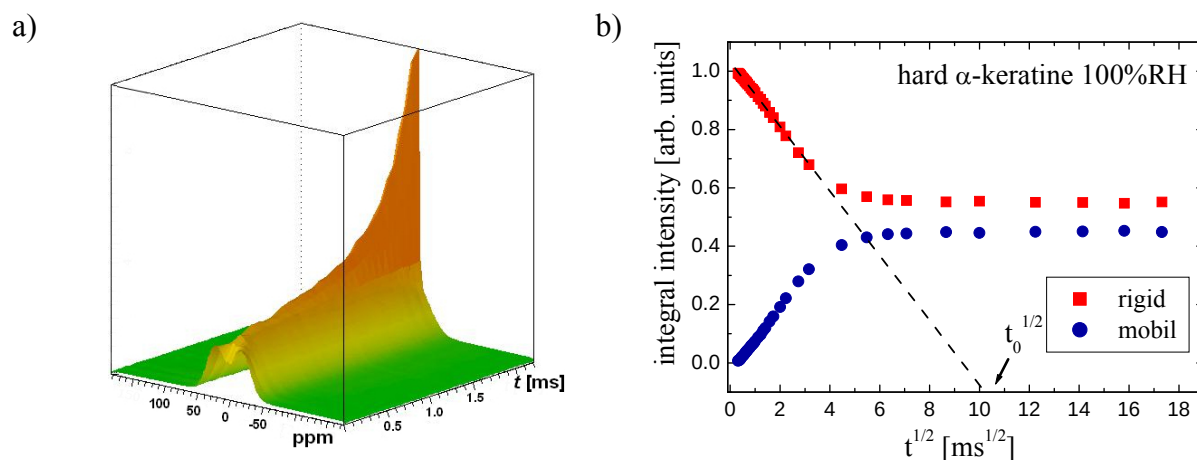


Fig. 7.4 a) Stack-plot representation of the ^1H spectra for Caucasian hair as a function of the diffusion time t . b) Decay and build-up spin-diffusion curves from normalized integral spectral intensities. The straight line describing the initial rate behavior intersects the horizontal axis at $\sqrt{t_0}$.

The domain size of the mobile fraction increases about six times with the moisture uptake (Fig. 7.5), which suggests large participation of water molecules, which plasticize the amorphous region of the keratin fiber [Pop1], to a cooperative movement. The increase of the domain size of the rigid fraction is less pronounced.

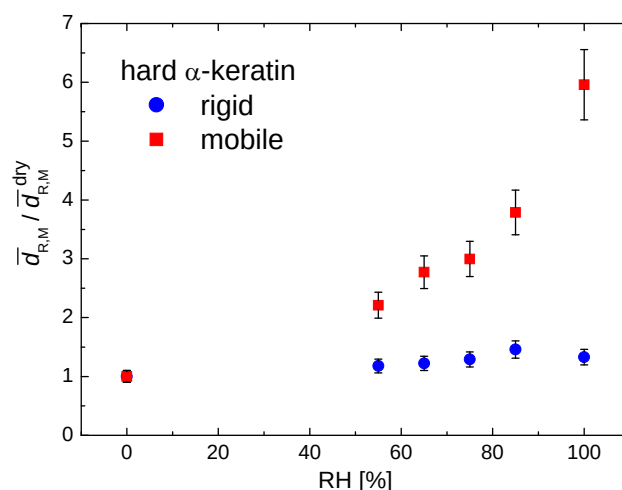


Fig. 7.5 The dependence of the rigid and mobile domain sizes of hard α -keratin as a function of relative humidity.

7.5 Conclusions

It has been put into evidence that the presence of water in hard α -keratin affects the morphology and the aminoacid side-chain dynamics due to the water molecules present in the keratin matrix and to the probable formation of an ordered (rigid) hydration shell around the keratin's intermediate filaments. Within the limits of experimental error, the concentration and the molecular mobility of the interfacial region do not change significantly with the hydration level, while both rigid and mobile fractions are affected. The presence of a water fraction with a relatively constant mobility could be also shown. The amount of this water fraction increases with the moisture content. The domain size of the mobile fraction and, at a lesser extent, that of the rigid fraction, increases with the moisture uptake, indicating the participation of most of the water molecules to the side-chains mobility.

Summing up, it has been shown that the water molecules absorbed by hard α -keratins contribute to the modification of the domain fractions, the size and the mobility of the rigid and mobile regions of keratin. It has been observed that a certain amount of water is present as such, probably accommodated in the voids of the matrix.

7.6 References

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General Conclusions

The results reported in this work are related to the development of new NMR methods and their applications to new high-performance polymer materials, biomolecules and biopolymers (fibrous proteins). A short summary of these novelties and outlooks are listed below:

1. The phase composition, the presence of the mobile and intermediate fractions in drawn UHMWPE Dyneema[®] fibers were reported for the first time for a relevant series of draw ratios. The changes in the domain sizes as a function of tensile strength were also reported from ^1H spin-diffusion data. For the first time thermally polarized ^{129}Xe was used for the characterization of the voids produced in Dyneema[®] fibers by uniaxial mechanical deformation.
2. Ultrafast 2D NMR spectroscopy was successfully applied to solid-state NMR under MAS. This result is expected to open a new field in NMR spectroscopy with many applications for polymers, biomolecules and biomaterials.
3. LASER hyperpolarized ^{129}Xe was used to investigate the exchange between the Xe atoms in a porous membrane and the free Xe gas. The kinetics of this exchange was studied by a fast EXSY NMR experiment.
4. A new NMR method based on the rotor synchronized stimulated echo was used for the measurements of residual dipolar couplings. The method has many applications in the field of soft solids, for instance, in studies of elastomers or gels.
5. For the first time, a correlation between the domain size measured by SAXS and ^1H spin-diffusion was reported in this thesis for an iPP/SiO₂ nanocomposite polymer. It was shown that NMR can characterize the interfacial region between the rigid and amorphous fractions, which is a unique feature of spin-diffusion NMR. The gradient in the chain dynamics at the interface can be measured and correlated with other properties of the polymer.
6. The correlation between morphological changes and chain dynamics in diblock copolymers was established by ^1H spin-diffusion and ^{13}C $T_{1\rho}$ measurements. The effect of the molar mass of each fraction in the considered diblock copolymer was also investigated.

7. A large set of classical and advanced multidimensional NMR experiments like REDOR, WISE, ^{13}C $T_{1\rho}$, ^{31}P wideline spectroscopy, and thermally polarized ^{129}Xe was used for characterization of lecithin, a model biomolecule.
8. For the first time, the interaction between water and hard α -keratin has been investigated by ^1H solid-state NMR. Phase composition, side-chain dynamics and domain sizes were measured for different values of relative humidity. The spin-diffusion has been analyzed in the initial rate approximation form which the domain sizes have been evaluated. These results open the possibility to investigate fibrous keratins under different conditions.

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Curriculum Vitae

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