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Summary of the PhD work of Alina Buda

Miss Alina Buda is working in my group as a PhD student since May 2001. During this time she obtained many interesting results related to the methodological development in the field of the spin-diffusion NMR and the characterization of different polymers, biopolymers and biomaterials. A short presentation of these results is given below.

1. Methodological development in the field of spin-diffusion NMR

The macroscopic properties of polymers are often determined by the existence of heterogeneities on different length and time scales. Typical examples for heterogeneous polymers are phase-separated and semi-crystalline polymers, polymer blends, block copolymers and organic-inorganic hybrid materials. While the primary structure of the macromolecular chain determines the local behaviour, the macroscopic properties often reflect the inherent heterogeneity like morphology, domain size, structure of grain boundaries, internal interfaces.

One established NMR method to investigate domain sizes and morphology of heterogeneous polymers is based on the magnetization-exchange after production of a z-magnetization gradient by a dipolar filter. These spin-diffusion experiments are suitable to investigate different aspects of structural heterogeneities in a broad range of spatial dimensions from 0.1 nm to about 200 nm.

1.1 The spin-diffusion process has been investigated in a model morphology system represented by three different domains with arbitrary sizes, diffusivities, and proton densities. General analytical solutions valid for the full range of spin-diffusion times were derived for an one-dimensional process. In the adopted model the nuclear magnetization transfer occurs from a source and flows into a finite sink via an interface. The theoretical approach was based on the use of the Laplace transformation. The integral intensities corresponding to each domain were evaluated, and a C++ program was written for their generation. The obtained solutions were tested for a poly(styrene-b-methylphenylsiloxane) diblock copolymer and semicrystalline poly(ethylene oxide) by predicting the domain sizes and comparing with the previously reported data. For the first time, the effect of the interface in terms of the size and the spin-diffusion coefficient on the spin-diffusion curves was directly investigated. The simulations showed that the presence of the

interface has a stronger effect on the signal obtained from the sink region than on the signal obtained from the source region. The value of the spin-diffusion coefficient in the interface has only a small effect on the spin-diffusion build-up and decay curves and therefore, an arithmetic average of the spin-diffusion coefficients in the source and sink is a good approximation for its value. The applicability of these solutions can be extended for studying the diffusion of liquids, and for mass or heat transfer in systems having the same morphology.

These results have been published in J. Phys. Chem. B [4].

1.2 A generalization of the solutions addressed above was made for taking into account the filter efficiency. This model can be, for example, very useful for investigating spin-diffusion process in an inhomogeneous magnetic field.

These results have been published in Solid State NMR [5].

1.3 General analytical solutions valid for the full range of spin-diffusion times were also derived for a process taking place in a cylindrical morphology composed of two domains. The integral intensities corresponding to each region show a complex dependence of domain sizes, spin-diffusion coefficients, and proton densities. The errors induced by the description of a spin-diffusion process in such a morphology by a multiplication of one-dimensional solutions were discussed.

A manuscript on this topic is in preparation [10].

1.4 Very often the heterogeneous materials have a complex morphology which is difficult to investigate by the classical techniques like for example X-ray methods. This is due to the fact that X-ray methods cannot provide direct access to information about the amorphous phase. For the first time an approach to characterize the complex morphology of polymers and fibres was introduced. It explores NMR spin-diffusion using a combination of dipolar filters based on the excitation of single and double-quantum coherences which select in separate experiments the magnetization coming from regions with different mobilities.

The MAPE (Magic and Polarization Echo) dipolar filter selects the magnetization from the mobile phases while that from rigid regions is destroyed. In the spin-diffusion experiments using a double-quantum (DQ) filter, by the appropriate selection of excitation/reconversion periods of the multiple-quantum coherences, the magnetization of the domains with stronger dipolar couplings in a heterogeneous sample will pass through the filter whereas that of the weaker dipolar couplings will be filtered out.

This approach was used to estimate the sizes of the rigid amorphous, the interface, and the mobile amorphous domains in polystyrene-poly(ethylene oxide) (PS-PEO) and poly(hydroxyethylmethacrylate)- poly(ethylene oxide) (PHEMA-PEO). For both systems the MAPE filter selects the magnetization coming from the PEO regions while the DQ filter selects the magnetization corresponding to PS and respectively PHEMA block.

The domain sizes measured by the double-quantum filter method are compared to those obtained using the traditional dipolar filter creating z magnetization in the mobile domains. For example, in the case of the amorphous PEO-*b*-PS diblock copolymer the long period of the lamellar morphology given by $d_l^{NMR} = d_{PS} + 2d_i + d_{PEO}$ has the value $d_l^{NMR} \approx 22 \pm 2 \text{ nm}$ measured using MAPE filter and $d_l^{NMR} \approx 20 \pm 2 \text{ nm}$ using the DQ filter.

Additionally, it was shown that information about the lamellar morphology of systems can be obtained independent of other techniques using such a combination of dipolar filters. This represents a big step forward in the field of spin-diffusion NMR.

These results have been already published in Solid State NMR [5].

2. Investigation of complex morphologies by spin-diffusion NMR

2.1 Nylon-6 fibres

Nylon-6 fibres have a morphology consisting of a complex distribution of mobile amorphous, less-mobile amorphous and crystalline regions. The value of their sizes as well as their spatial distribution influence directly the macroscopic properties of the fibres. Therefore, a knowledge of these microscopic distributed heterogeneities is required in order to engineer materials with the desired properties.

Samples produced with different winding speeds and draw ratios have been investigated using spin-diffusion experiments. Due to the fact that the fibres absorb water during the manufacturing process they have been kept in deuterated water for about two weeks.

The experimental approach involved a combination of spin-diffusion experiments employing the MAPE and the DQ dipolar filters. The particular set up of the spin-diffusion experiment in which the source of magnetization is selected in the mobile amorphous domains allows us to explore only some aspects of the complex morphology of the Nylon-6 fibers. The obtained data were interpreted based on a structural model which proposes the existence of aggregates of fibrils. The mobile

amorphous phase is situated at the surface of aggregates of fibrils and is separated from these aggregates by an interface. The detected magnetization transfer proceeds in a direction along the diameter of the fibrils. The mobile amorphous phase has domain sizes in the range of 3 - 4.5 nm for the investigated Nylon-6 fibers and it depends on the processing conditions. A similar dependence is observed also for the sizes of the aggregates. For instance, drawing the fibres to DR = 4.5 leads to a decrease in the aggregate size of about 20%. Additionally, the average number of fibrils per aggregate was estimated to be in the range of 4 – 10 for the investigated samples.

The above type of spin-diffusion measurements provides only global information even if the aggregates have a well-defined structure according to SAXS. Inside an aggregate the less-mobile amorphous domains separate the fibrils so that the fibrils have a lamellar structure with alternating crystalline and less-mobile amorphous domains.

To obtain a more detailed picture of the morphology of Nylon-6 fibers, spin-diffusion experiments were conducted with a double-quantum filter. In this situation, the source of the z magnetization was selected mainly in the crystalline regions. The magnetization-exchange from selected crystalline domains to less-mobile amorphous regions along the fibrils and between the fibrils was simulated with the help of a three-dimensional solution of the spin-diffusion equation approximated by a product of one-dimensional analytical NMR signals which correspond to a lamellar morphology. This allows the measurement of domain sizes of crystalline and less-mobile amorphous domains along the fibrils as well as the diameter of the fibrils and the inter-fibril distance. The changes detected in the domain size dimensions with the processing conditions show the same trend as the data from wide-angle X-ray diffraction and small-angle X-ray scattering.

The results obtained in the spin-diffusion experiments with a MAPE filter have already been published in J. Phys. Chem. B [4] while those based on a DQ filter have been accepted by ChemPhysChem [6].

2.2 Diblock copolymers

The domain sizes of the rigid amorphous, interface and mobile amorphous regions of a serie of poly(ethylene oxide)-*block*-poly(hydroxyethylmethacrylate) (PEO-*b*-PHEMA) diblock copolymers with different molecular weights were estimated using

^1H spin-diffusion measurements employing a MAPE dipolar filter. The correlation of the lamellar long period $d_{long} = d_{mobile_amorphous} + 2d_{interface} + d_{rigid_amorphous}$ with the molecular weight show a dependence of $d_{long} \propto M_w^{0.64}$. This result indicates good agreement of the experimental data with the theoretical prediction $d_{long} \propto M_w^{2/3}$. Additionally, the dimensions of the interface show small variations with the molecular weight.

A manuscript on this topic is in preparation [9].

3. Heterogeneity of chain dynamics in confined thin lipid films

In the last years supported thin lipid films have attracted a lot of attention due to the increasing number of applications. They represent, for example, a relatively compatible structure for the development of new types of electrochemical sensors and biosensors with a fast response in time (on the order of a few seconds) and with high sensitivity (for example, nanomolar detection limit). Understanding the effects that the surfaces and the confinement have on the chain dynamics of the lipid films is a central need for engineering improved devices.

The molecular dynamics heterogeneities of lecithin films of controlled thickness ranging from a monolayer to submonolayers in submicron cylindrical pores of different diameters were investigated by ^1H magnetization-exchange NMR. The magnetization gradient in this experiment was created using a double-quantum dipolar filter. Three main regions exhibiting different chain dynamics were detected. The magnetization-exchange decay and build-up curves were interpreted based on an one-dimensional spin diffusion process in a three domain morphology. The speed of the magnetization transfer inside each region is characterized by an average spin-diffusion coefficient.

The obtained results show a strong dependence of the spin-diffusion coefficients on the surface coverage, pore size and temperature. The surface induces ordering of the lipid molecules such that they adopt different anchoring directions depending on the surface coverage (which is directly related with the concentration of the lipid in the solution absorbed on the pores) and the pore size. At small concentrations the results suggest that the molecules lie flat on the surface. By increasing the concentration the molecules adopt a tilted anchoring direction while for higher concentrations the fatty chains point in an axial direction. This behavior is not

only a characteristic of the lipid films but also of polymers and liquid crystals in interaction with surfaces.

The pore size shows also an important effect on the dynamics of the fatty acid chains. Decreasing the pore size from 200 nm to 20 nm leads to an increase of the residual dipolar couplings as reflected in the values of the average spin-diffusion coefficients. This suggests that in smaller pores elastic deformations can be presented.

An adhoc Gaussian distribution function of the ^1H residual dipolar couplings was used to quantify the effect of various parameters on the molecular dynamics of the mobile region of the fatty acid chains. The results indicate that the heterogeneity of the chain dynamics is higher for the concentrations where the molecules adopt a tilted anchoring direction, in pores with higher dimensions and at higher temperatures. The dependence of the spin-diffusion coefficients and of the width of the distribution function on surface coverage, pore size, and temperature shows that the surface inducing order and the geometrical confinement affect the dynamics of the entire molecule.

The described method can successfully be applied to obtain a better understanding of the effect of the interaction between different types of polymer materials, lipids and liquid crystals with surfaces.

These results have been already submitted to J. Phys. Chem. B. [8].

4. Shape memory polymers

Biodegradable polymers are an important class of synthetic biomaterials that are widely used in temporary therapeutic applications such as wound closure, tissue regeneration and drug delivery. Among the bioabsorbable polymers developed thus far, polyglycolide, poly(lactide), and their copolymers constitute promising materials for use in the field of surgery and pharmaceuticals. Additionally, these type of copolymers have a "memory" that allows them to be deformed into a temporary configuration and then to be restored to the original parent geometry by applying heat in few seconds.

To design polymers with suitable properties for a given application, an understanding of the structural characteristics, molecular dynamics and the mechanisms responsible for changes in physical properties associated with hydrolytical degradation is requested. Therefore, we have carried out solid-state

NMR studies of amorphous copolymers of *L,L*-dilactide and diglycolide. Different NMR techniques like the measurement of ^1H , ^{13}C spectra, $T_{1\text{H}}$, double-quantum build-up curves, and WISE were employed. The effects of the monomer ratio, molecular weight, and the UV-irradiation time on the structural and dynamical properties as well as on the degradation rate of the copolymers were investigated.

These results are the subject of two manuscripts [13, 14].

5. Ordered tissues

The role of proton exchange between water and proteins has been the subject of intensive work over the past few years. The interaction between collagen and its water of hydration is of special importance since the mechanical properties of connective tissues like cartilage, tendon, and ligaments dependent on this interaction. Therefore, understanding this interaction can be a requirement for the development of treatment strategies and for engineering of artificial tissues.

In this study a new method to assign the peaks of the exchangeable collagen protons and to measure the exchange rates of these protons with water was introduced. The method implemented under MAS (5kHz spin rate) uses the WATERGATE sequence for on resonance peak suppression in the selection and detection period. On the basis of experiments where H_2O was replaced by D_2O , the peaks of the exchangeable protons were identified to be in the range of 5.5 - 8.7 ppm. An assignment of the peaks from this region was made based on previous experiments on peptides. The exchange rates of the NH and OH protons were estimated. The results suggest that the magnetization-transfer between collagen and water in tendon proceeds mostly via chemical exchange of NH protons.

A manuscript on this topic is in preparation [15].



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