Investigation of Slow Dynamic Processes in Natural Abundance Polymeric Systems by Novel 1D-MAS Exchange NMR Methods

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Summary: We introduce a recently developed class of Solid-State NMR experiments for the investigation of slow dynamic processes in organic solids. These 1D-MAS exchange experiments do not require selective isotopic labeling and can be performed with standard solid-state NMR hardware. The data are easy to analyze and provide selective information about the correlation times as well as about the topology (jump angles etc.) of dynamic processes in different sub-units of the molecules. We present data for Poly(n-butylmethacrylate), PBMA, between the glass transition temperature T_g and the $\alpha\beta$ splitting temperature, in order to demonstrate the advantages of these 1D-MAS methods.

Introduction

The characterization of slow dynamic processes with correlation times τ_c in the millisecond range plays an important role for the understanding of function and properties in organic materials, such as polymers. Relaxation methods, i.e. mechanical and dielectric spectroscopy are well established methods for such investigations. However, they either rely on a molecular probe (e.g. the electrical dipole moment for dielectric spectroscopy) and can thus provide information about this particular site of the molecule only, or the assignment of the experimentally detected dynamic process to the molecular structure is not exactly known. Thus, it is not possible to straightforwardly correlate the different molecular sub-units of a given sample (for example, the main and the side chain in a polymer) to the experimentally detected dynamics.

Solid-state NMR (Nuclear Magnetic Resonance) is a powerful, yet demanding tool for such investigations. It provides molecular resolution by either selective isotopic labeling or by the intrinsic spectral resolution of MAS (Magic–Angle Spinning) NMR spectra (see Fig.3), as well as information about the orientation of the sample nucleus. The latter is encoded in the NMR frequency by anisotropic NMR interactions. Since molecular

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processes often involve reorientations, these exchanges of the orientation of the probe nucleus with respect to the external magnetic field is detected as exchange of the NMR frequency in a properly designed experiment.

To detect slow processes, the well-known schema of Exchange NMR must be applied. In such experiments, the NMR frequency, hence the orientation of the sample nucleus, is detected before and after an adjustable period (mixing period τ_m), see Fig.1. For $\tau_m \ll \tau_c$, there is no exchange of orientations of the sample nucleus and thus, the NMR frequencies before and after τ_m are equal while for $\tau_m \geq \tau_c$, these frequencies are different. Exchange-NMR methods are basically two-dimensional experiments that are very demanding in terms of machine time.

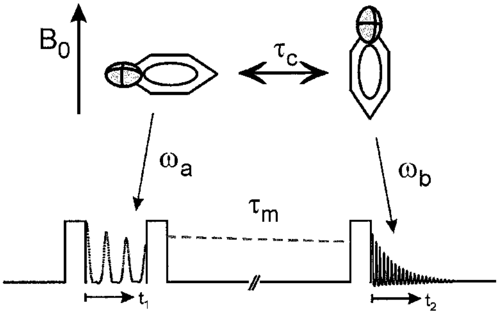

Fig.1: Principle of the NMR-Exchange experiment

For the efficient investigation of slow molecular dynamics in organic material, the NMR method of choice should meet the following requirements:

- Because selective isotopic labeling is not feasible for most of the problems, the method should work with samples at natural isotopic abundance. To achieve molecular resolution, this inevitably requires the application of MAS experiments.
- The method should use standard NMR equipment, a simple setup procedure of the experiment and should provide easy access to the dynamic parameters from the NMR data since each additional requirement hampers the application of NMR tools. Many recently introduced NMR methods rely on the presence of sophisticated NMR hardware, like high-speed MAS-NMR probes or high-end electronic hardware and/or involve sophisticated data processing procedures, sometimes requiring demanding numerical simulation of NMR data.
- The method should provide a good signal (signal-to-noise-ratio) within reasonable

experimental times, to allow a unambiguous determination of dynamic parameters and to enable the study of systems with a complex dynamics like polymers.

Experimental

All the requirements listed above are met by the recently developed 1D-MAS exchange methods trODESSA (*t*ime-*r*everse *O*ne-*D*imensional *E*xchange *S*pectroscopy by *S*ide-band *A*lternation) [1] and CODEX (*C*enter-band *o*nly *D*etection of *Ex*change) [2], see Fig.2. In both methods, the length of mixing period τ_m has to be synchronized with the rotation period of the spinning sample, T_R. τ_m is embedded in-between two evolution delays by which the frequency of the probe nucleus, hence its orientation, is encoded. For $\tau_m \ll \tau_c$, a normal MAS spectrum is recorded while if a dynamic process has changed the orientation of the probe nucleus during τ_m, a decay of the signal intensity in the MAS spectrum is recorded, see Fig.4. For CODEX, additional radio-frequency (R.F.) pulses are inserted in the evolution delays (k times in Fig.2) to amplify the frequency encoding. The latter permits experiments at higher MAS rates, however, the additional pulses and longer evolution delays deteriorate the signal intensity.

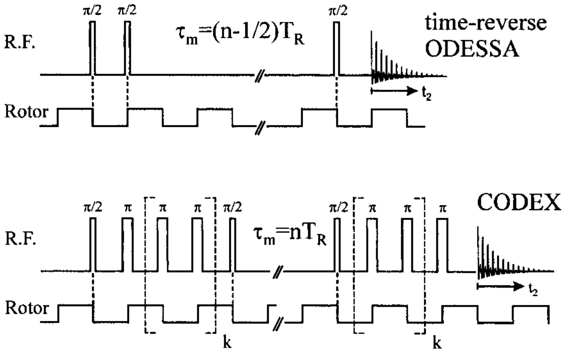

Fig.2: Pulse sequences for trODESSA and CODEX

Care should be taken to select the proper experiment for the actual case. Generally spoken, trODESSA is preferable if the dynamic process involves large-angle reorientations, if the MAS can be set to rates smaller than the anisotropic line widths ("slow MAS"), and in all cases where the signal-to-noise is a critical issue. In contrast, CODEX experiments must be applied whenever the experiment is performed under "fast MAS" conditions, if the dynamic process involves small-angle reorientations only and/or when more detailed information about the topology of the dynamic process (jump angles etc.) are wanted.

To determine dynamic parameters, trODESSA or CODEX experiments has to be performed for a sufficiently large number of logarithmically spaced values of τ_m. The line intensities vs. τ_m for all resolved resonances in the MAS spectrum can be plotted as shown in Fig.4. For jump-like processes, these plots are decaying functions and are proportional to the well known correlation function of motion, thus providing an easy assignment of the NMR data to the dynamic parameters. Since many relaxation processes in polymeric systems, in particular the dynamic glass transitions (α relaxation), can be approximated by stretched exponential (KWW) function [3], the experimentally observed exchange decay is described by:

$$S(\tau_m)/S_0 = (1-a) + a e^{-\left(\frac{\tau_m}{\tau_c}\right)^{\beta}} \tag{1}$$

where the parameter β ($0<\beta\leq 1$) is a measure for the widths of the τ_c distribution and the parameter a contains information about the topology of the dynamic process. However, the latter can only be extracted by assuming motional models and performing numerical simulation. Thus, we will restrict ourselves to qualitative discussions here. All experimental data $S(\tau_m)/S_0$ were corrected for T_1 and spin diffusion [4,5]. The number of π-pulses in the evolution periods of the CODEX experiments were chosen to meet the asymptotic level.

Sample

We will demonstrate the methods introduced above by the investigation of the amorphous polymer PBMA at T=40°C, close to its glass-transition temperature T_g=25°C.

Fig.3 shows the chemical structure as well as the assignments of the different carbons to a standard MAS spectrum. It is clear that the latter provides sufficient spectral resolution to selectively investigate the main and side chain as well as carboxylic group that links the latter. The experiments presented below were performed using a standard 7mm CP-MAS probe. Typically, about 5000 accumulations were added for each τ_m value of the exchange experiments, resulting in an overall experimental time of about two to three days for each experiment.

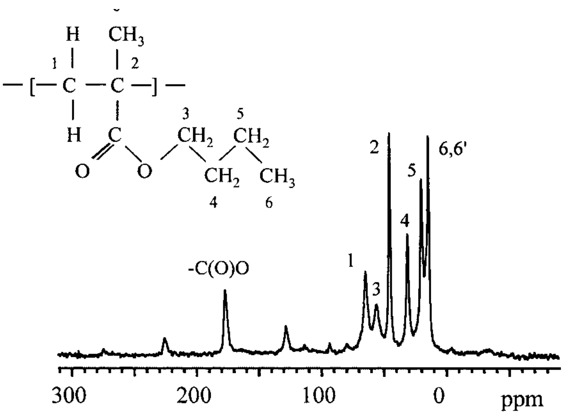

Fig.3: Monomeric unit of PBMA and MAS spectrum. $\nu_0(^{13}C)=100MHz$, $\nu_{ROT}=4.9kHz$

Results and Discussion

Fig.4 shows plots of the line intensities vs. τ_m for different carbons representing the main (C2) and side chain (C4) as well as the carboxylic group (COO). Note that the former are results obtained by a CODEX experiment while the latter is a trODESSA data set, due to the smaller signal intensity of the COO line which makes the signal-to-noise-ratio a critical issue. In contrast, the investigation of the aliphatic resonances C2 and C4 requires the application of additional pulses during the evolution periods of the CODEX

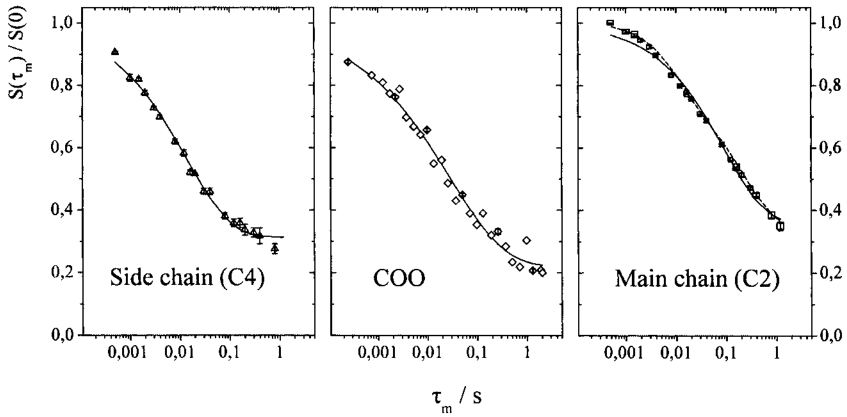

Fig.4: Exchange decays for the indicated carbon resonances of PBMA. T=40°C

experiment (k>0 in Fig.2).

The solid lines in the plots are fits to the data by a stretched exponential function, Eq.(1). While the data for the carboxylic and for the side chain (C4) are approximated reasonably well by Eq.(1), a single KWW function obviously does not describe the exchange decay of the main chain carbon (C2) satisfactory well. There is a systematic deviation of the fit from the experimental data at $\tau_m \approx 1...20$ms that suggests the existence of multiple dynamic processes. This assumption is supported be independent results from relaxation spectroscopy showing also two co-existing processes, the dynamic glass transition α and the local mode β, in this frequency-temperature range for PnBMA.[6] Assuming a sum of two KWW decays (dashed line in Fig.4) we obtained from the data for the main chain carbon C2 correlation times of about 10 and 200 ms, respectively. Note that only the very good signal-to-noise-ratio (see the error bars in the plots) of our NMR data permits the unambiguous assumption of a second process in C2 data for PnBMA at 40°C and a stable multi-parameter fit.

Table 1 summarizes the dynamic parameters obtained from the fit to the data of Fig.4. A comparison with the Arrhenius diagram of PBMA from dielectric spectroscopy (cf. Ref.5) shows that the signal for the side-chain carbon C4 and the fast process τ_c' in the main-chain carbon C2 reflect the β process while the slower process of C2 is the α process, i.e. the conventional dynamic glass transition slightly below the $\alpha\beta$ splitting. The dynamics of the carboxylic carbon cannot be assigned to neither the main nor to the side chain. Although its wide distribution (small β value) suggests contributions of α and β processes, these processes cannot be told apart (as for the main-chain carbon C2). This shows that the dynamics of the COO carbon is somewhat different and independent from those of the main and side chain carbons.

Table 1. Dynamic parameters obtained from fitting the data of Fig.4.

	C2	C4	COO
a	0.19	0.67	0.78
τ_c	0.011	0.013	0.028
β	0.97	0.49	0.39
a'	0.47		
$\tau_{c'}$	0.21		
β'	0.65		

To gain more inside into the dynamics of PnBMA our 1D-MAS experiments have to be repeated for different temperatures. Additional information can be obtained by evaluation of the parameter *a*, too. Work along these lines is in progress and will be published elsewhere.

Summary and Outlook

We have shown that the recently developed 1D-MAS exchange NMR methods trO-DESSA and CODEX permit the investigation of slow dynamic processes in organic solids by standard NMR equipment without selective isotopic enrichment of the samples. Data are presented for PnBMA, demonstrating that the different dynamics of various molecular sub-units can be distinguished. The obtained parameters can be assigned to correlation times and widths of their distributions. Potential fields of applications of 1D-MAS methods are the search for correlations between the molecular dynamics and the biologic activity in biopolymers [5], the performance of functional polymers, or optimization of solid electrolytes.

Acknowledgement

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