

Application note

Fast Field Cycling Relaxometry: Application to Polymers

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Introduction

The Field Cycling technique permits NMR relaxation measurements to be carried out as a function of magnetic field strength B_0 , thus allowing important information on molecular dynamics to be obtained. In fact, all information on molecular dynamics contained in the spectral density function can be inferred by the NMRD curve which reports T_1 or $R_1=1/T_1$ versus the Larmor frequency ω ($\omega=\gamma B_0$, γ is the gyromagnetic ratio). Therefore, NMR Field Cycling Relaxometry turns out to be very useful for investigating the dynamic behavior of polymeric materials allowing a detailed description of the amplitude and characteristic times of the molecular motions over a wide frequency range. Generally the interpretation of NMRD experimental data in terms of dynamic parameters requires the use of suitable models of motion, which result as helpful in providing a correlation between the parameters with physical properties and information on structural features of molecules on both the global and local scale.

Furthermore, the possibility of setting and controlling the sample temperature, over a large range of values in combination with the NMRD profile makes FFC-Relaxometry a very important source of information concerning molecular motions characterized by temperature-activated frequencies according to Arrhenius behavior.

Herein we show the applicability of the SPINMASTER FFC2000-1T for the acquisition of NMRD profiles of some important polymeric materials.

The method

Field Cycling instruments provide a reliable and useful method for measuring the R_1 dispersion curve ($R_1=1/T_1$ as a function of the applied magnetic field strength), called Nuclear Magnetic Relaxation Dispersion (NMRD) profile, over several decades of Larmor frequency (*i.e.*, different applied magnetic fields).

A basic field cycling experiment consists of a three step cycle, illustrated in figure 1.

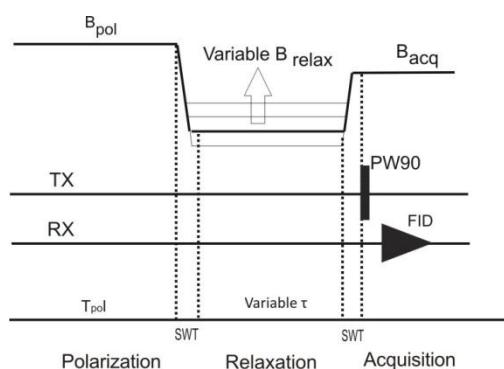


Figure 1. Basic scheme for FFC NMR relaxometry. B_{pol} is the polarization field applied in the time interval T_{pol} ; B_{relax} is the relaxation field applied for variable times τ ; B_{acq} is the acquisition field, PW90 is the 90° RF pulse applied to retrieve the observable FID, and SWT is the switching time.

- Polarization:** The sample is pre-polarized to improve signal Intensity (B_{pol}).
- Relaxation:** the field is switched to a lower value (B_{relax}) to allow the sample to relax during a time τ .
- Acquisition:** The field is switched to the detection field (B_{acq}) for signal acquisition (FID).

FFC –NMR and Polymers

Several reviews and books have appeared in the literature on the relaxation mechanism and theory of FFC-NMR and polymers, nevertheless, this note does not attempt any theoretical interpretation of the data collected herein in terms of molecular dynamics.

The focus of this document is to show the potential advantages of Fast Field Cycling Relaxometry which, allowing NMR relaxometric measurements to be obtained as a function of frequency, is highly beneficial for discrimination between various molecular dynamics models. In fact, it is the goal of many experiments to establish the connection between macroscopic and microscopic behavior. The data may just signal a generic difference in chemo-physical properties or assist the understanding of fundamental mechanisms: the macroscopic properties determining the possible applications are strongly dependent on microscopic processes. Therefore a quantitative investigation of motions on molecular levels can provide fundamental information on features at the basis of technology.

The great advantage of this technique is that it is sensitive to motional processes on different time scales, mainly from a few kHz to several hundred MHz, allowing molecular motions with correlation times ranging from 1 ns to few μ s to be probed.

The time-dependent magnetic field NMR technique, becomes particularly interesting within the lowest Larmor frequency limit, where other conventional NMR experiments present severe signal-to-noise ratio degradation.

The availability of scanning molecular motion on a frequency scale of several orders of magnitude in a continuous fashion by field cycling NMR relaxometry permits some noteworthy findings, which could be interesting for potential use in quality assessment and off-line process monitoring, to be obtained:



- The shape of the relaxation dispersion remains a feature characteristic to the type of polymer (figure 2).

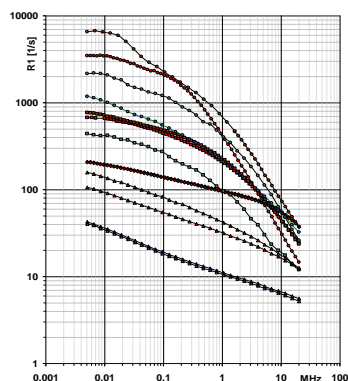


Figure 2 NMRD profiles of some different families of elastomers (S. Sykora, and . A.L. Segre's team are gratefully acknowledged)

- T_1 or $R_1=1/T_1$ particularly at low frequencies was demonstrated to be extremely sensitive to small amounts of solvent or un-polymerized monomers, while no effect is seen at high field (figure 3).

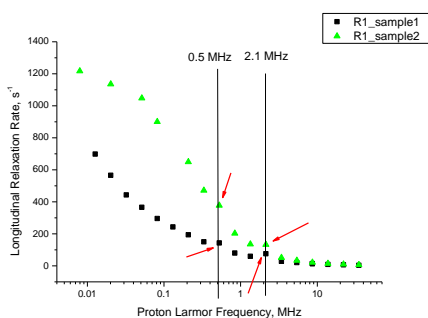


Figure 3 NMRD profiles of two polyamide sample with different hydration state.

In Figure 3, the occurrence of the so-called “nitrogen glitches” (0.5 MHz and 2.1 MHz) are indicated: these are due to the interaction between protons and quadrupolar nuclei (^{14}N).

- The dependence of T_1 dispersion on mechanical stress is mostly of fundamental interest, but can be exploited to investigate samples undergoing stress-strain experiments (figure 4).

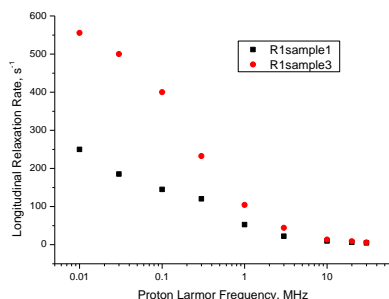


Figure 4. NMRD profiles of the same polymer obtained from two different mechanical processes.

Figure 4 represents two NMRD profiles of the same polymer obtained from two different mechanical processes. This reflects in substantial differences seen in the dispersion profiles of the two samples.

The differences are clearly evident at low fields of investigation, where the components of slow molecular dynamics have greater efficiency in the relaxation processes.

- Through T_1 relaxation decay it is possible distinguish various components of motion (multi-exponential).

In heterogeneous or anisotropic systems when several different motions are present, NMR measurements made as function of frequency can in principle give information about the amplitude and characteristic times for each of the motions. Furthermore different components may be encountered if protons belong to different molecules or if they are involved in different physical states. The different contributions can rise from intra/inter-molecular proton interaction, amorphous/crystalline part, fast/slow motion. The following graphics show the dispersion profiles of spin-lattice relaxation rate ($1/T_1$) of the two components derived from the discrete bi-exponential fit. Watching those we can see that the multi-exponential behavior becomes much less evident at higher relaxation fields (Figure 5)

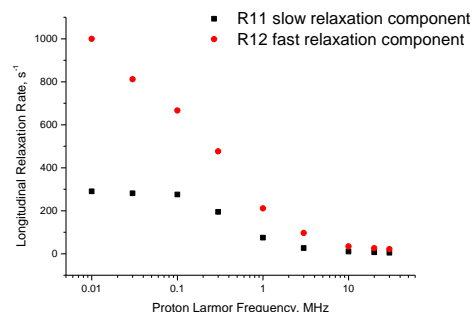


Figure 4 NMRD profile of the two components derived from the discrete bi-exponential fit.

In complex multiphase systems, when the decay constants have values close enough to each other, a continuous distribution may be a better representation of the proton spin population and the Laplace transformation is the most widely accepted algorithm used to describe the NMR decay.

In NMRD-D, the distribution of relaxation times is measured at different Larmor frequencies (*i.e.*, different applied magnetic fields) and the variation in those distributions can be examined as a function of the frequency to monitor aggregation and the collective effect (Figure 5).

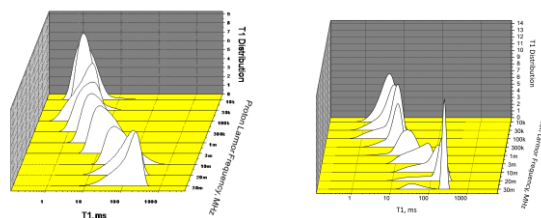


Figure 5. Comparison of two NMRD-D of two polymer samples (sample 3 on the left and sample 1 on the right) with different chemical structures.

From the distributions we can get the mean T_1 , thus obtaining a NMRD profile weighted on the distribution. The results are shown in the Figure 6.

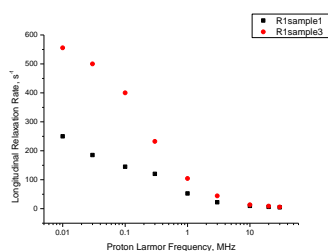


Figure 6. NMRD profiles weighted on the relative distributions of Figure 5. The differences are clearly evident at low fields of investigation.

Temperature dependence

When temperature- and frequency-dependent NMR relaxation rates are available over a large dynamic range, NMR relaxometry is able to provide a comprehensive picture of the relevant dynamic processes characterized by temperature-activated frequencies (activation energy, Arrhenius and non-Arrhenius behavior, as well as correlation times and correlation effects).

Figure 7 shows NMRD profiles of a Polyisoprene sample at several temperature values in the range from 10 to 50 °C (a) and the relative Arrhenius plots (b).

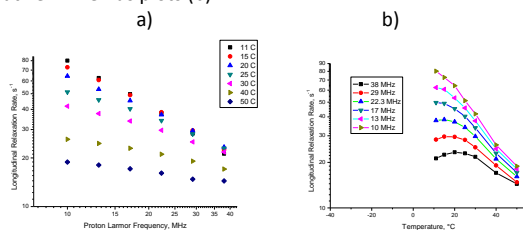


Figure 7 a) NMRD of polyisoprene sample at several temperature values; b) Arrhenius plots.

A qualitative analysis of the R_1 experimental curves, reported in Figure 7b reveals a regular trend characterized by the presence of a peak whose corresponding temperature seems to decrease with decreasing Larmor frequency. Since the relaxation rate maxima shift to higher temperatures at higher frequencies, low NMR frequencies and a large temperature range are important to distinguish different motions.

Within the temperature range investigated only the 35 MHz curve has a well delineated peak. The experimental data can be analyzed taking into account single motional process according to the Arrhenius equation.

Figure 8 shows the longitudinal relaxation rate data (R_1) at 35 MHz as a function of temperature, and the relative fitting curve based on a simple BBP relaxation model and a modified Arrhenius equation.

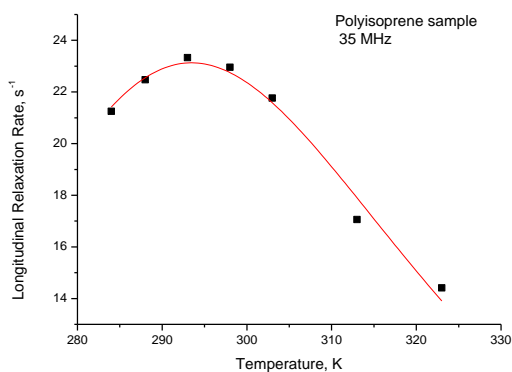


Figure 8 Longitudinal relaxation rate data ($R_1=1/T_1$) at 35 MHz as a function of temperature. The red line is a fitting curve by means single motion process model and a modified Arrhenius equation.

By the means fitting model it is possible to evaluate the activation energy (E_a) of motion and the relative attempt frequency ν_{att} (τ_{∞}^{-1}):
 $E_a \sim 20 \text{ KJ/mol}$
 $\nu_{att} \sim 10^{-13} \text{ s}^{-1}$.

These parameters are presumably due to the reorientation motion of the methyl groups.

Hetero-nuclei

It is also possible to carry out FFC NMR relaxation experiments directly on hetero-nuclei with low receptivity and detectability, and to evaluate the relative NMRD profile (other than ^1H also ^2H , ^{13}C , ^{19}F and ^7Li nuclei).

Figure 9 shows the Deuteron T_1 decays of a polymeric fuel cell membrane measured directly on a solid sample at three different magnetic fields (0.0023 T, 0.023 T and 0.5 T).

The decays show an evident multi-exponential behavior particularly at low field. The relaxation data were evaluated with discrete and continuous methods.

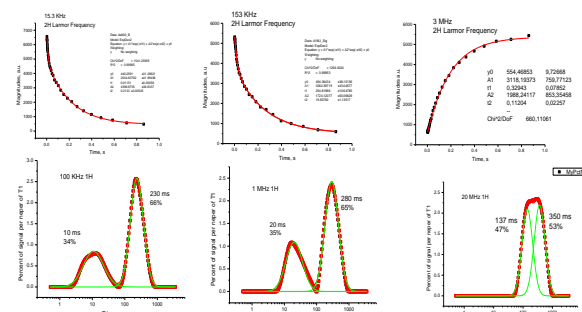


Figure 9 Distribution curves obtained by UPEN; the green lines indicate the Gaussian de-convolution curves. The de-convolution process allows calculation of the relative percentage of the components and the evaluation of peaks corresponding to the relative T_1 .

Conclusion

In this report some applications of FFC Relaxometry were reported to show the applicability and the potential of the technique on polymeric material whose chemico-physical properties cannot be understood without knowledge of their molecular mobility.

SpinMaster FFC 1T is a unique instrument designed to measure the field dependence of T_1 from earth field to 1 Tesla (42.6 MHz).

The great advantage of this technique is that it is sensitive to motional processes on different time scales, mainly from a few kHz to several hundred MHz, allowing molecular motions with correlation times ranging from 1 ns to few μs to be probed.

FFC NMR relaxometry technology is now at a level of sophistication and maturity where industrial applications are possible. It is extremely versatile and can serve as an instrument for basic R&D, applied R&D and process monitoring. Applications for FFC NMR relaxometry appear in practically every physical and engineering science discipline.

SpinMaster FFC 1T

