NMR Relaxometry vs. Spectroscopy

Magnetic resonance (NMR) spectroscopy is the absorption of electromagnetic radiation by a nucleus, typically in the MHz/ radio-wave frequency (RF) range. An RF-pulse causes a change in the molecular 'spin state' that can be observed for a period of time, during which the spin states are relaxing back to equilibrium. For solid-state spectroscopy relaxation times can be as short as a few microseconds and for liquid state spectroscopy they can be on the order of seconds or minutes.

While both NMR relaxometry and spectroscopy use magnetic resonance principles and involve the same absorption of radio waves, NMR relaxometry provides information about the bulk properties of a sample being measured, whereas spectroscopy gives chemically specific information about each part of a chemical's molecular structure. NMR relaxometers are typically operating at "low field" frequencies (e.g. 20 MHz for ^{1}H) and are often used in quality control and process optimization. Applications include xylene solubles (XS), copolymer (C2) and mechanical properties determination (polypropylene), MFR or density (polyethylene), but also solid fat content (SFC) in food, determination of hydrogen content in fuels or moisture detection. Detectable nuclei include protons (hydrogen), fluorine (^{19}F) and phosphorous (^{31}P). NMR relaxometers are robust instruments that can be used in challenging environments, e.g. polymer manufacturing plants, whereas NMR spectrometers are very sensitive to their environment and require especially equipped laboratories.

NMR spectroscopy is used for research-oriented applications as an analytical technique as it provides detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. Traditionally, NMR spectrometers operate at higher frequency ranges, typically between 200 and 1200 MHz (^{1}H frequency), but during the last decade several benchtop units were introduced at mid-range frequencies (< 100 MHz). High frequency NMR spectrometers are spacious, require cryogens (liquid helium and nitrogen) for operation and typically require to be operated by experts in lab environments.

In NMR spectroscopy the user typically needs a frequency spectrum, so the initial NMR response, the "Free Induction Decay" (FID), needs to be mathematically transferred from the time-domain to the frequency-domain which is accomplished using a Fourier Transform (FT). For this reason, NMR spectroscopy is sometimes referred to as "FT-NMR" to distinguish it from NMR relaxometry for which no Fourier Transform needs to be performed as the FID signal can be analyzed directly in the time-domain.

What is NMR relaxometry?

Relaxometry refers to the measurement of relaxation variables in nuclear magnetic resonance data, i.e. amplitudes and relaxation times. The latter can refer to either spin-lattice relaxation (T_1) or spin-spin relaxation (T_2). Nuclear magnetic moments in NMR are used to measure specific chemical and physical properties of bulk materials. LexMar Global's NMR analyzers are relaxometers optimized for analysis of polyolefins in manufacturing plants and can be employed on-line in hazardous as well as non-hazardous areas, but also off-line in laboratories. For these applications typically T_2 relaxation is employed for sample analysis.

After FID acquisition there are several ways to analyze the data and extract information contained in the FID. One is to determine intensity ratios at two points which is a great way to get a coarse result for a two-phase system. An alternative is performing an inverse Laplace transform on the FID to determine rapid vs. slow relaxation which is the method of choice for complicated systems. For the determination of polyolefin bulk-properties the method of choice is curve fitting, as polyolefins are three-phase systems consisting of a crystalline, an amorphous and an intermediate fraction. This is the method typically used by LexMar Global. Apart from strength of the magnetic field, the main difference between NMR spectrometers and relaxometers is the homogeneity of the magnetic field. For FT-NMR the homogeneity needs to be very good. In order to achieve this, a room temperature shim-system is employed. When properly adjusted this allows for a very good resolution and allows to distinguish between tiny differences in complicated spectral systems.

The relaxation rate of a given spin depends on the mobility of the microscopic environment. Relaxation times and relaxation rates are inverses of each other. Relaxation dynamics depend on the strength of the applied magnetic field (e.g. 0.45 T for a magnet operating at 20 MHz ^{1}H frequency). Strong magnetic fields cause an increased sensitivity on fast dynamics while low fields lead to an increased sensitivity on slow dynamics. Because of this, how the relaxation rates vary in relation to the magnetic field strength serves as a fingerprint of the microscopic dynamics.

NMR spectrometers and relaxometer

While relaxometry measurements can theoretically be performed on both relaxometers and spectrometers, there are certain advantages to use a relaxometer: first, a relaxometer allows for measurements of liquids and solids at the same time, while a typical spectrometer is used for analysis of liquid systems. There are also spectrometers dedicated for solid-state analysis, but these cannot handle mixtures of liquids and solids either. The fact that a relaxometer magnet is less homogeneous compared to a spectrometer magnet turns out to be an advantage for bulk property measurements. There is a trade-off between probe quality and electronic dead times. Spectrometer probes typically feature a high quality-factor (Q) and are optimized for solutions. They are designed to achieve a high signal-to-noise ratio but relatively long dead times, whereas dead times for relaxometers are designed to be short to allow for acquisition of solids or crystalline fractions of FIDs.

LexMar Global relaxometers are specifically designed for polyolefin analysis. The principle of operation is to determine crystallinity. Therefore, by design the probes feature a low Q and short dead times as well as a large volume for polymer samples to be representative in a production environment. In contrast, FT-NMR volumes are typically small to accommodate for tiny substance amounts in R&D environments.

Polymer samples are conditioned automatically within the relaxometer. Analysis temperature is optimized for polyolefin samples and heating times are short, so results can be obtained as quickly as possible to allow for process optimization (one data point every 10-15 minutes). On-line NMR allows for process feedback, so the sample point is close to the reactor in a hazardous area. Alternatively, for off-line NMR a sample needs to be taken out of the process manually and transported to the lab.

Sample preparation is minimal for relaxometry. No solvents are needed and sample analysis is automatic as soon as the samples are introduced into the analyzer. For on-line NMR the whole sampling and analysis process is fully automatic with no human interaction needed. The analyzer works 24/7, easily with >97% uptime. In either case results are automatically transmitted to LIMS and DCS systems as needed. In contrast, high resolution FT-NMR requires deuterated solvents and careful sample preparation. Automatic sample preparation robots and exchangers exist, but systems are complicated and require maintenance and expertise. Spectrometers cannot be used in hazardous areas, so the main benefits of on-line systems cannot be achieved.