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Solid State NMR

Maria Ines Bruno Tavares

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Abstract

The nuclear magnetic resonance (NMR) spectroscopy is a very powerful tool in the chemical characterization, both in solution and in solid state. With the development of NMR spectrometers more potent field, employing radio frequency pulse, provided the development of studies on materials, especially amorphous materials. Thus, there was a need to develop techniques to obtain spectra in solid state with high resolution in comparison to those obtained in solution. Therefore, the study of polymers and polymeric materials could be developed quickly as a result a lot of information about the structure-property could be obtained with more details. The use of NMR in the solid state has become particularly important in the study of amorphous materials, as well as in the study of crystal structures, and permits us to detect different constituents present in material. This chapter covers the basic solid-state NMR techniques that provide important information on sample molecular behavior because they are powerful and versatile tools to evaluate polymer and complex materials like nanomaterials.

Keywords: NMR, solid-state, polymer, nanomaterials, relaxation times

1. Introduction

Solid-state nuclear magnetic resonance (NMR) consists of several techniques, which are distinguished by different pulse sequences and generate different responses on the sample, allowing obtaining data on different time scales. This makes the development of new analytical methods for the study of polymer materials interesting. The solid-state analyses differentiate the solution by two main factors; the first is signal width. In the solid state, the signals are broader than solution, concerning to polymers due to the high-molecular weight and monomer ordination; among other factors, the signals are wider. The second point concerns the type of response obtained; in the solid state, the number of information obtained is greater than solution. When the material is insoluble or has soluble difficulties, the study of

structure-property relation is of great interest because the search for responses with respect to homogeneity, phase dispersion, and intermolecular interaction between components is of great importance.

1.1. Nuclear magnetic resonance experiment

In the NMR experiment, a sample is placed in probe in a strong magnetic field, denominated B_0 ; if this sample presents magnetic moment (μ), its nuclear spins magnetize and at the excess of spin population, called magnetization (M_0), is applied for a radio frequency (RF) pulse by a radio frequency emission (B_1) field, the magnetization is excited by transfer to the xy plane. When the RF emission is turned off, nuclear spins tend to return to the steady state since this state has less energy, occurring in a process called relaxation. In this process, two types of relaxation occur simultaneously: one denominated transverse or spin-spin relaxation, which occurs in the xy plane and has a time constant $-T_2$, and the other called longitudinal or spin-lattice relaxation that occurs along the axis z and is characterized by the time constant $-T_1$. The NMR signal is detected after the withdrawal of radio frequency, with a process of free induction decay (FID) of the radio frequency, which results from the free precession of the nuclear spins, upon its return to steady state.

The NMR relaxation processes with time constants T_1 and T_2 are governed by fluctuating magnetic fields associated with molecular motion. The relaxation process that determines the T_1 values involving energy absorption, since this process is enthalpic. The temporal evolution of the transverse relaxation is fundamentally different from longitudinal, and it corresponds to a loss of phase coherence between the individual magnetic moment process in it, and, thus an increase of entropy. In many cases, solid sample loss phase coherence initially created by B_1 is due to direct interactions between the spin moments of individual [1–10].

1.2. High-field NMR

1.2.1. Solid-state NMR analyses

The solid-state NMR is constituted by several distinct pulse sequences, which generate different responses on the sample, allowing obtaining data on different time scales. This makes possible to develop new analytical methods for the study of complex solid materials [1–5], as polymer nanocomposites.

The analysis of the complex materials in the solid state differentiates the analysis in solution by two main factors: the first is the signal width. In the solid state, the signals are broader than in solution and especially for polymers due to their high molecular weight and mere ordination, among other factors, the signals become even wider. The second point concerns the type of response to be obtained in the solid state the number of information to be obtained is greater than in solution [11–14]. However, when the material is insoluble or has soluble difficulties, the study of the structure-property relation is of great interest because the search for responses with respect to homogeneity, phase dispersion, and interaction between the components is of great importance.

a. Nuclear magnetic resonance signal line width

Generally, the spectra obtained in solution generate narrow signals best resolved comparing to solid-state signals, due to the isotropy of the chemical shift, since all interactions as shielding, dipolar coupling, and indirect coupling depend on the orientation of the local environment in nuclear magnetic field B_0 and when the samples are in solution, these effects are compensated. However, they are dependent on the nature of the sample and the external magnetic field strength applied [7–10].

In solids, there is usually little movement relative to the liquid. However, most samples (except single crystals) have a substantial molecular orientation range of line width. This fact comes from the anisotropy of the chemical shift as well as the strong dipolar interaction between the hydrogen nuclei and carbon-13. The nature of the sample and the type of nucleus to be observed are also two points of fundamental importance to the spectral resolution in solid state.

b. Solid-state nuclear magnetic resonance response

The type of answer you want to get on a specific material or on a polymeric system may be a reason why those must be analyzed by solid-state NMR. Information on the molecular dynamics is of great interest for answers about the correlation structure-molecular-dynamic property.

The problem of signal line width in NMR solid-state spectra led to the development of techniques that allow them to obtain signals in the solid state the narrowest possible, like liquids. Along with the information to be obtained on the material, different techniques are performed to analyze more different polymer systems.

1.2.1.1. High-resolution solid-state NMR basic theory

The Hamiltonian that governs the analysis involves a solid sum of different Hamiltonians, according to expression 1.

$$\mathbf{H}_{\text{NMR}} = \mathbf{H}_{\text{Z}} + \mathbf{H}_{\text{RF}} + \mathbf{H}_{\text{CSA}} + \mathbf{H}_{\text{D}} + \mathbf{H}_{\text{J}} + \mathbf{H}_{\text{Q}} \quad (1)$$

where \mathbf{H}_{Z} is the Zeeman effect; \mathbf{H}_{RF} is the radio frequency effect; \mathbf{H}_{CSA} is the chemical shift anisotropy; \mathbf{H}_{D} is the dipolar interaction between hydrogen nucleus and the carbon-13 nucleus; \mathbf{H}_{J} is the coupling constant; and \mathbf{H}_{Q} is the quadrupolar moment.

When one observes spin nuclei $\frac{1}{2}$, as carbon-13 (^{13}C), for example, the Hamiltonian that promotes more interference in the signal enlargement are \mathbf{H}_{CSA} e \mathbf{H}_{D} . Improving the resolution of the signals in the NMR spectra obtained in the solid state requires techniques to eliminate factors that cause this signal enlargement [10–14]. Thus, techniques were developed using methods that mathematically eliminate these effects.

1.2.1.1.1. Magic angle spinning (MAS)

The strong dipolar interactions between hydrogen nuclei and carbon-13, facilitated by the internuclear distance between them and the restricted mobility of the chains and the

anisotropy of the chemical shift generate signals in very wide solid, with line width of 20 kHz order. The elimination of the dipole-dipole interaction generates a decrease in the signal line width of 5 kHz, and the elimination of the anisotropy of chemical shift width of the signals decreases to 100 Hz, making possible the detection of signals. Both the dipolar interaction and the anisotropy of the chemical shift dependence have with the term $3\cos^2\theta-1$. The elimination of these two effects occurs when the solid analyzes are performed by rotating the sample at high rotational speeds (each nucleus suitable for a given magnetic field) in a sample introduction probe angle corresponding to the amount of 54.74° , able to eliminate the term $3\cos^2\theta-1$, aligned with a strong decoupling of the hydrogen nucleus generating a significant narrowing of the line width in spectrum.

The employed pulse sequence is simple:

$$\begin{array}{l} \text{hydrogen} \quad \quad \quad \text{decoupling} \\ \text{nucleus observed} \quad [90^\circ x \rightarrow \text{FID} - t]n \end{array} \quad (2)$$

where t is the time interval between 90° pulses (delay) and n is the number of scans.

The time t is variable and it is directly related to the relaxation time of different types of nuclei that are analyzed. Thus, variations in this parameter allow studies that provide information about the molecular mobility of the sample and the time of spin-lattice relaxation.

All nuclei that undergo the phenomenon of resonance can be analyzed by this technique. However, for the observation of nuclei that have quadrupole moments, line widths are so large that the signals have no resolution. However, for nuclei having dipole moment, this technique generates high-resolution spectra. It should be considered that for high-molecular weight materials such as polymer, for example, the chemical structure can be defined by this technique. However, a fine or detailed microstructure structure cannot be observed as they are well resolved by the NMR solution techniques. Because in the carbon-13 solid state analysis the signals broadened comes from the dipolar interactions and the chemical shift anisotropy, generating large signals that contain all molecular information's.

Note that using the MAS technique can obtain quantitative spectra solid. However, the long analysis time, comes from the high values of the spin-lattice relaxation times of the different nuclei, mainly rare spin. It makes this type of spectrum replaced by spectra expressing or representing only a portion of the sample. Therefore, variation in spectral parameters of this pulse sequence provides information about the increased mobility of a sample region, for example, a mixture of polymers, polymers, composites, amorphous, and nanocomposite materials. Thus, a greater number of applications of this technique can be obtained, when seeking information about the homogeneity, compatibility, and purity of polymers or any material samples.

The analysis of materials by the MAS technique using a small interval between pulses (ms) can detect only one region or the region that has the highest mobility. This variation in the MAS technique enables, in the case of amorphous polymers, that is, ethylene-co-vinyl acetate (EVA), identifies the region of increased molecular mobility, or distinguishes the mobility of different areas, which cause changes in the properties of the material [6–10].

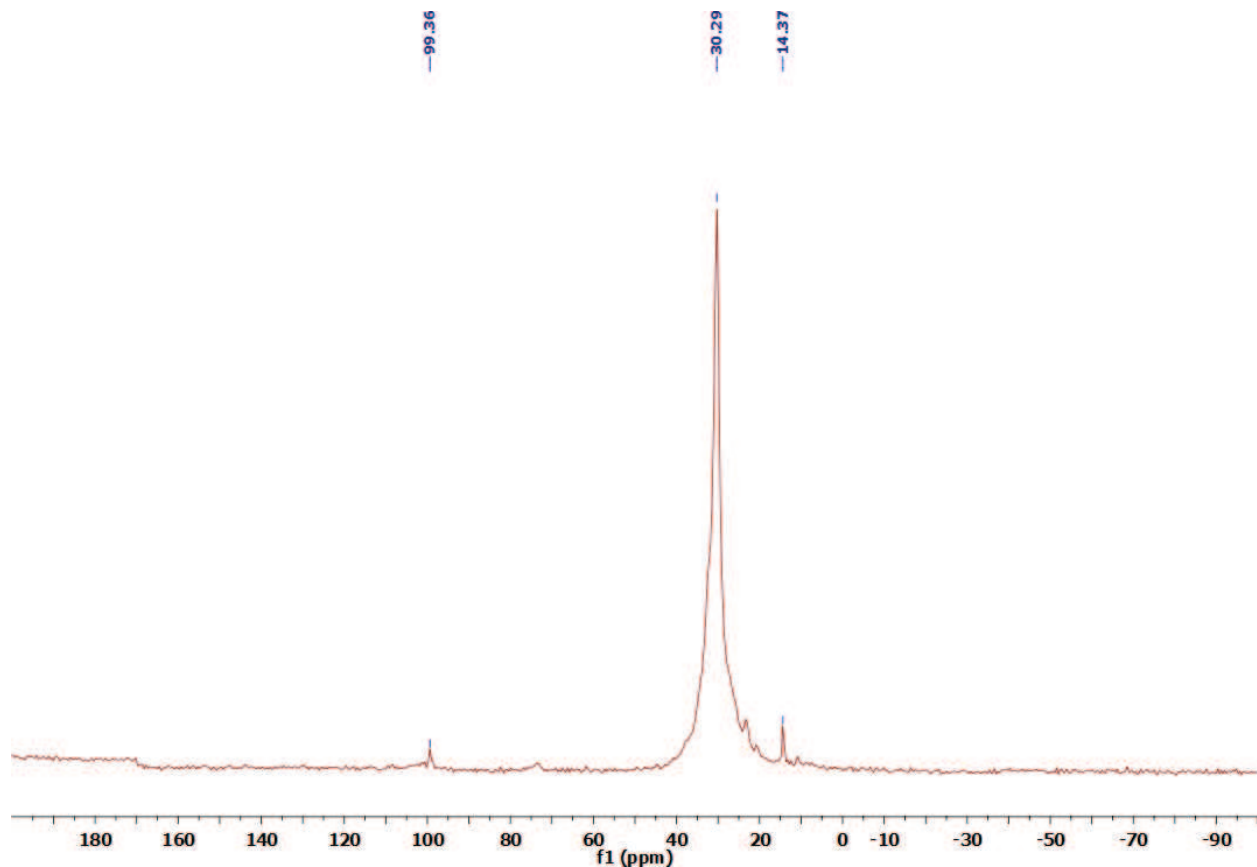


Figure 2. Solid-state NMR C-13 MAS spectrum of powder EVA.

Figure 3 shows the powder EVA CPMAS C-13 NMR spectrum, with 1 ms of contact time. It already showed two signals: one located at short chemical shift, centered at 30.7 ppm referring to mobile region and the other one located at 32.3 ppm due to the segments of rigid region.

One type of solid-state NMR studies is to use a comparison between ^{13}C NMR spectra obtained by techniques MAS and CPMAS, which can first show the different regions of the samples. One example was showed in the literature, which exhibits the MAS and CPMAS solid state NMR spectra of seed flour bourbon mango spectra [15, 16]. It shows that in these spectra have at least two segment areas of different molecular mobilities, and it may also a third due to the interaction of these two domains that may not be detected in this type of measurement.

1.2.1.1.3. Variable contact time (VCT) during polarization transfer

This technique generates a variation of contact times during the cross-polarization experiment, leading to a series of ^{13}C CPMAS spectra with different contact times, and through this experiment, one can obtain some important information, such as heterogeneity of the sample, material stiffness, different types of domains, and the value of the hydrogen spin-lattice relaxation time in the rotating frame ($T_{1\rho\text{H}}$). This parameter can be obtained from the intensities decay of carbon-13 nucleus during the cross-polarization transfer experiment, according to the changes in the contact time, since the hydrogen nucleus is the one that controls this relaxation process. **Figure 4** exhibits the variable contact-time experiment for powder EVA.

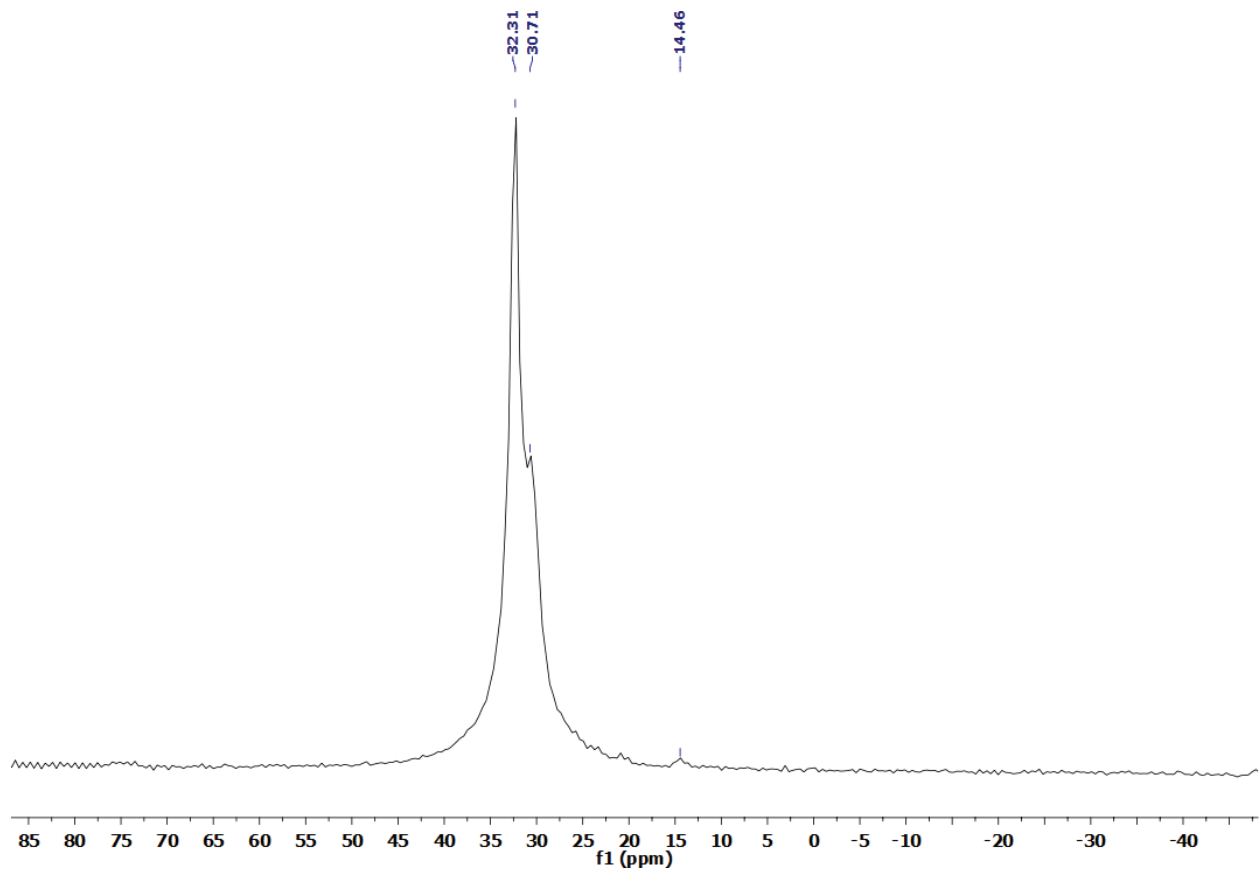


Figure 3. Solid-state NMR CPMAS C-13 NMR spectrum of powder EVA.

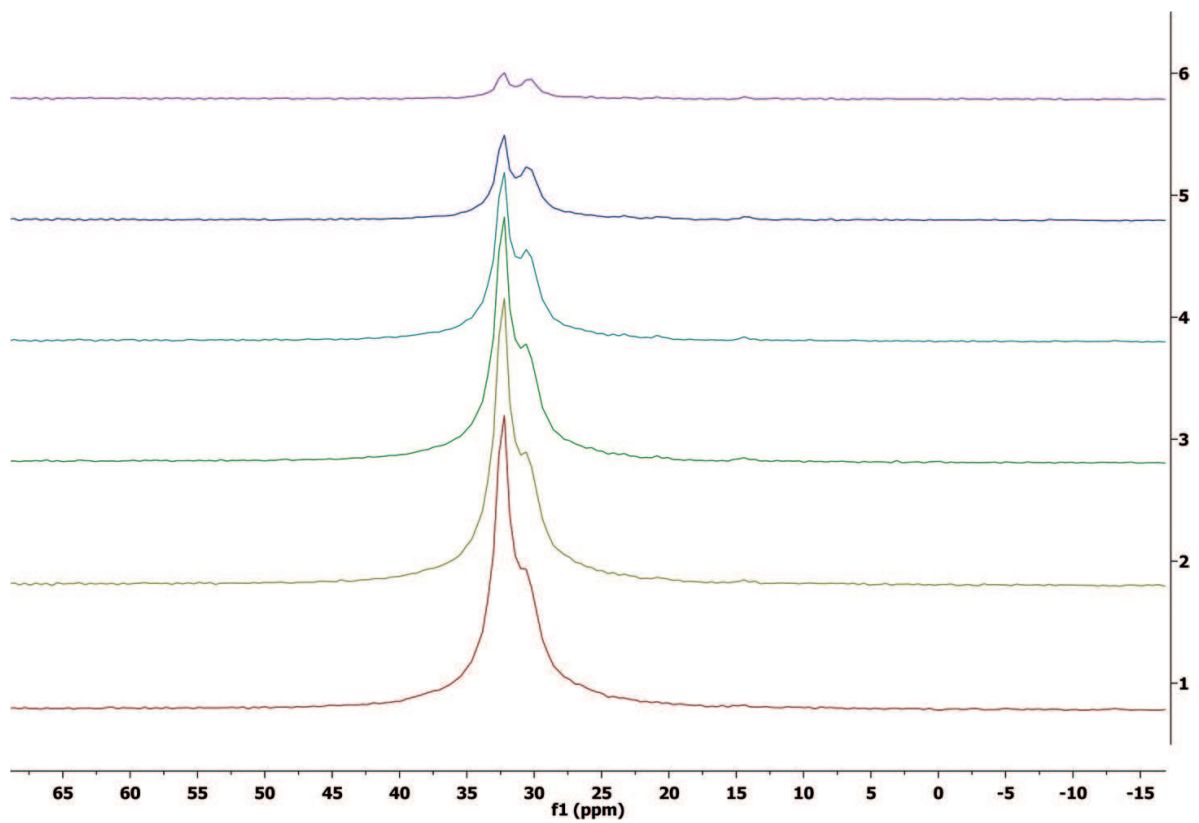


Figure 4. Variable contact time experiment of powder EVA.

This experiment shows the decay of both resolved carbon types detected from CPMAS with contact-time variation, showing the rigid part of the sample and part of the mobile one with the increase in the signal related to the CH_2 of the nonrigid phase.

2. Case study

2.1. Example of the determination of $T_{1\rho\text{H}}$ for polymer nanocomposites based on poly(3-hydroxy butyrate) (PHB)

In this study, it was evaluated the $T_{1\rho\text{H}}$ for the PHB/silica (PHB/S) systems contain different proportions of silica. All samples were obtained through solution casting, and the films after being dried were out into the rotor, the analyses were carried out at 30°C , and the values of this parameter are listed in **Table 1**.

From the data listed in **Table 1**, just a small proportion of silica affects the polymer, promoting a formation of a new material. Therefore, the relaxation data for the samples containing 0.5 or more silica exhibit a similar behavior, promoting an increase in this parameter comparing to pure PHB indicating that a new material with good dispersion and distribution of the nanoparticle in the polymer was obtained. The limit of silica is 0.5%, and no more is needed since no change in the $T_{1\rho\text{H}}$ for all carbons was detected. The evaluation of this parameter is not very much used for polymer nanocomposites yet. Therefore, studies have been already published by the group for other systems, as blends and composites [24], and show the behavior of these polymer materials [25].

Sample	$T_{1\rho\text{H}}$ (ms)			
	C = O	CH_2	CH	CH_3
PHB	13	26	31	17
PHB/S 0.2	15	19	27	19
PHB/S 0.5	33	32	34	32
PHB/S 0.75	31	32	34	30
PHB/S 1.0	31	31	34	30

Table 1. $T_{1\rho\text{H}}$ data for the PHB/S systems, containing different proportions.

3. Low-field NMR

In low-field NMR equipment due to low intensity and homogeneity of the magnetic field, the chemical shift cannot be used to discriminate between different molecules. The nuclear relaxation processes occurring in the nuclear magnetic resonance phenomenon inherent to

spectroscopy are spin-lattice and spin-spin relaxation times; however, they provide detailed information about the molecular dynamics. These relaxation times influence from the structural and microstructural quantitative determination by the study of molecular dynamics. The relaxation processes are associated to the time constant for these processes: T_1 , spin-lattice relaxation time, and T_2 , spin-spin relaxation time. In the low-field NMR, the relaxation parameters T_1 and T_2 for the hydrogen nuclei that constitute the samples can be measured directly, using the pulse sequences for such experiments and are widely used to characterize the types of molecular segments present in the samples and the interactions between them [15–20]. The time T_1 is associated with the return of the nucleus excited by the absorption of radiation to the equilibrium. While T_2 relaxation is related to the inverse of the half-width of the signal and occurs due to the loss of phase coherence in the precession of the nucleus excited about the direction of the applied magnetic field [1–3].

The relaxation times determined by NMR offer detailed information on the molecular mobility of a material. Thus, one could detect the formation of rigid and flexible segments, plasticization or antiplasticization process, and any other change in the molecular dynamics of the sample or comparing the variation of the molecular mobility of structures from the same type of material, but of different origin. The time of relaxation times T_{1H} and T_{2H} can be measured in a wide temperature range and identifying small differences in similar structures.

3.1. Determination of T_1

The inversion-recovery pulse sequence is the most accurate technique for measuring the relaxation time spin-lattice process. The T_{1H} relaxation time is measured in the frequency of magnetic field generated by the external magnetic field. This relaxation must do with the return of the excited nuclei to its ground state after removal of the excitation frequency, and therefore, it allows to evaluate the molecular mobility of a material, global compatibility and homogeneity, as well as processes and plasticization [1–3, 10–15]. In this process, the excess energy is emitted to the lattice in the form of dipole interaction since there is a lowering of the enthalpy of the nuclear spin system. The return to the magnetization to the equilibrium state is usually exponential, and is a first order process with constant speed, R_1 , and time constant T_1 .

The applied pulse sequence is described below:

$$\text{Observed nuclei: } [180^\circ_x - \tau - 90^\circ_x]_n \quad (3)$$

where τ is a time interval between 90 pulses.

The relaxation time T_{1H} reports on the molecular dynamics of materials. In the case of starches and starch flour, for example, this parameter is sensitive to the formation of domains or segments and structural changes in the range 15–50 nm.

3.2. Determination of T_2

The proton spin-spin relaxation time, T_{2H} , in principle, can be obtained by measuring the width of the NMR signal at half height. However, the inhomogeneity of the magnetic field

causes the magnetization of the different nuclei processes at different rates when removing the RF and a time τ is needed to wait, which is chosen depending on the mobility of the sample; however, this inhomogeneity is refocused after an application of a 180° pulse, generating a single magnetization [1, 15, 16]. The pulse sequence normally used is Carr-Purcell-Meiboom-Gill (CPMG), which contains a train of pulses [1–5].

This relaxation time, and the time constant of spin-lattice relaxation reports about molecular mobility of materials in the molecular level, thereby assess overall molecular dynamics and segmental. The T_2 H parameter corroborates data obtained by T_1 H and sometimes can inform more detail of the material behavior under observation, if this have some regions or segments containing high-molecular mobility.

In several studies that involve the evaluation of molecular mobility of materials, specially using the NMR relaxometry, it was normally employed the measurements of relaxation times spin-lattice and spin-spin and evaluate the T_1 and T_2 times constants of both relaxation phenomena, respectively. This comes from the fact that these parameters are sensitive to dynamic processes that occur at different frequency ranges. Thus, T_1 parameter measures the relaxation of the magnetization component parallel to the external magnetic field, being sensible to fast movements that are sensible to the movements of first order (MHz). The T_{1p} relaxation parameter is measured in low frequencies in the range of tens of kilohertz [1, 7, 17–23].

4. Final comments

In the solids, there is a restricted molecular movement comparing to liquids. However, most of the samples range have a substantial molecular orientation of the line width. This fact stems from the anisotropy of the chemical shift as well as the strong dipolar interaction between the hydrogen and carbon-13. The nature of the sample and the type of nuclei to be observed are two points of fundamental importance to the spectral resolution. The type of answer you want to get on a specific material may be a reason why it must be analyzed by solid-state NMR. Information on the molecular dynamics is of great interest for answers about the correlation structure-molecular-dynamic property. The line width in NMR solid state spectra led to the development of techniques that allows obtaining signals in the solid state most narrow possible, like liquids. Along with the information to be obtained, different techniques are performed to analyze the more different polymer systems.

Author details

Maria Ines Bruno Tavares

Address all correspondence to: mibt@ima.ufrj.br

Federal University of Rio de Janeiro, Professor Eloisa Mano Macromolecules Institute,
Rio de Janeiro, Brazil

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