

FFC APPLICATION NOTE: POLYMERS

Fast Field Cycling applied to polymers: tacticity and molecular weight

^aM. Pasin, ^aR. Steele, ^aG. Ferrante, ^bN. Hari^aStelar Srl, Via E. Fermi, 27035 Mede (PV), Italy^bSASTRA Deemed University, Tirumalaisamudram, Thanjavur, 613401, India

Introduction

In this application note, we show the power of the Fast Field Cycling NMR relaxometry (FFC) technique in obviating practical difficulties and further demonstrate the utility of FFC in addressing one of the key properties of polymers, that is, tacticity, through a case study on the most widely used and well-known industrial polymer, polypropylene.

“**Tacticity**” of a polymer refers to the relative stereochemistry of adjacent chiral centres within the macromolecule (polymer). This has important implications on its physical and mechanical properties as the regularity of the polymer structure will influence its degree of rigidity (crystalline long-range order) and flexibility (amorphous long-range disorder), as well as its melting point and solubility.

Polymers may be classed as **isotactic**, **syndiotactic** or **atactic**: **isotactic** polymers are made up of macromolecules with all the chiral substituents on the same side of the backbone chain. For example, the methyl substituent groups of the backbone in isotactic polypropylene will all be “meso” (e.g. all R-methyl or all S-methyl groups). **Isotactic** polymers are indeed usually semi-crystalline in character; **syndiotactic** polymers are characterized by alternating substituents along the backbone (in polypropylene this is R-methyl, S-methyl, R-, S-, ... etc.). Syndiotactic polymers tend to be crystalline in character; Atactic polymers have a random configuration of substituents along the backbone and are amorphous in character as the random positions of the substituents along the backbone make it difficult to crystallize (atactic polymers can be of industrial importance as they can be “glass-formers”, such as atactic polystyrene).

Polymers are chosen for use by industry depending on their physical and mechanical properties and thus it is important to be able to analyze the tacticity of a polymer. Indeed, solution and solid-state NMR have become indispensable tools for characterization of polymers. To understand polymer structure-function

relationships, several methodologies are being deployed by analysts.

Historically, polymer analysis by NMR has been hampered by poor spectral resolution which is owed to structural features of repeating units. Albeit the power of two-dimensional techniques to resolve spectral resolution, practical difficulties in terms of sample preparation, usage of exotic and expensive solvents, operational temperature during analysis have to be overcome. For example, polyvinylfluoride having average MW of 80,000 requires benzene-d₆ as a solvent and an operational temperature of 65 °C. For certain classes of polymers, operational temperature can even go as high as 160 °C.

Herein, we reveal initial studies showing that FFC NMR relaxometry is a promising method of analysis for the tacticity of polypropylene and for defining the average molecular weight of polypropylene chains.

Case study: tacticity of the polypropylene (PP)

The aim of this case study was to assess the potential of the FFC technique to discriminate commercially available isotactic polypropylene (PP) from atactic PP (unfortunately, syndiotactic polypropylene was no longer available from the same commercial source). We considered the following samples:

- ISO250K: isotactic PP with molecular weight 250K (from Sigma-Aldrich: Product Number: 427888)
- Amorphous: atactic PP (from Sigma-Aldrich: Product Number: 428175)
- MIX: a mixture of two PP's composed of 20% amorphous and 80% ISO250K melted together at over 260 °C

FFC measurements were carried out at a constant temperature of 25 °C using a Stelar SPINMASTER. A volume of 1 cm³ of sample was used in a 10mm diameter flat-bottomed NMR tube. No solvents were required to dissolve the samples (measured as is). Measurements

were performed at the following magnetic fields:

- 1 MHz
- 0.5 MHz
- 0.250 MHz

The duration of each experiment was around 15 minutes. In **FIG. 1**, we show an example of the magnetization decay for the amorphous sample and the fitting line (in red) obtained using the bi-exponential fitting function:

$$Y = A \cdot \exp(-\tau/T1_a) + B \cdot \exp(-\tau/T1_b)$$

The magnetization decay is displayed as normalized magnetization points versus TAU, where TAU is the time interval during which the magnetization relaxes at the specified magnetic field (*i.e.* Relaxation field = 1; 0.5; 0.250 MHz).

All the data-sets were fitted by this model comprising two independent components: a slow-relaxing longi-

FIG. 1:
 The plot shows the experimental points of the magnetization decay of the Amorphous sample measured at 1MHz and fitted using a bi-exponential algorithm (red line).

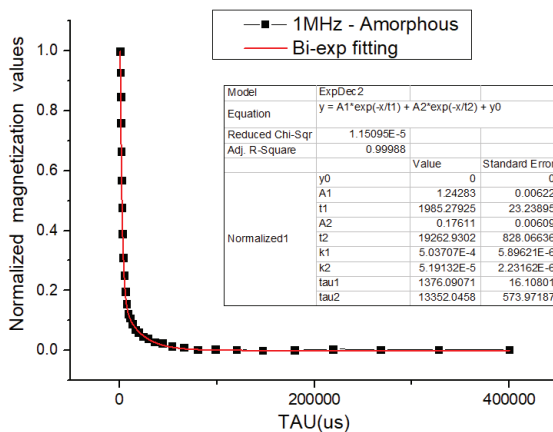


FIG. 2:
 NMRD profiles for the fast-relaxing longitudinal relaxation component of the samples.

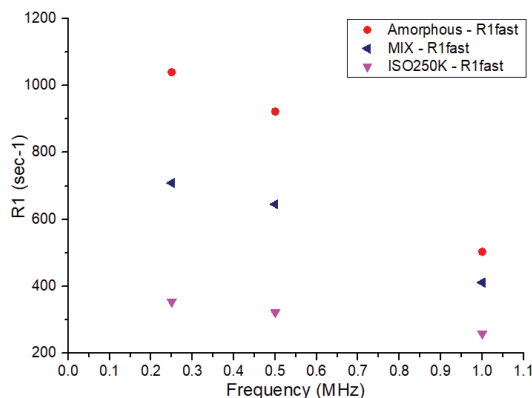
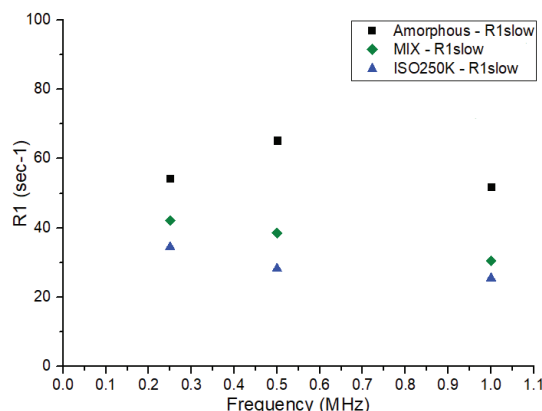


FIG. 3:
 NMRD profiles for the slow-relaxing longitudinal relaxation component of the samples.



tudinal magnetization component characterized by a longer $T1_a$ and a fast-relaxing component characterized by a shorter $T1_b$. Results are reported as NMR dispersion (NMRD) profiles in **FIG. 2** and **FIG. 3**.

For better visualization of the differences between the fast (**FIG. 2**) and slow (Fig.3) components of the longitudinal relaxation, we display them in two different plots. Both the fast and slow components of each sample can be distinguished from those of the other samples (**FIG. 2** and **FIG. 3**). Particularly, from a comparison between **FIG. 2** and **FIG. 3**, it is easier to distinguish the samples relying on their fast-relaxing component. The difference between the fast-relaxing components of the samples is much larger than the difference between the corresponding slow-relaxing components. Moreover, for the fast-relaxing components, the difference between the R1s of the samples increases as the magnetic field decreases. In conclusion, results show that the FFC method allows the discrimination between all the samples and, particularly, it makes possible to characterize the isotactic sample.

In fact, the NMRD profile of a sample can be considered as its “fingerprint” as shown in **FIG. 4**, which displays the NMRD profiles of several polymers from a Stelar in-house study. It shows that every NMRD

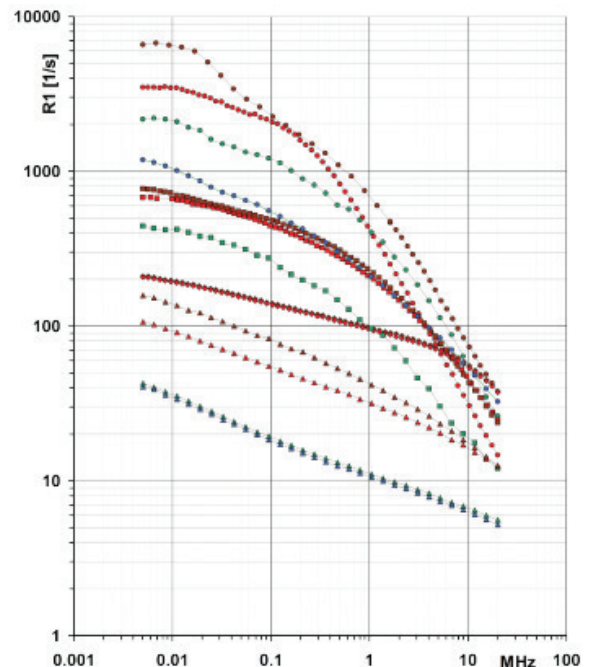


FIG. 4:
 Listed from top down at 0.01 MHz:
 CIRCLES: Brown: Isobutylene-isoprene; Red: Styrene-butadiene, anionic; Green: Polychloroprene cis; Blue: Ethylene-propylene rubber.
 SQUARES: Brown: Styrene-butadiene; Red: Styrene-butadiene, radical; Green: Polyisoprene trans.
 DIAMONDS: Brown: Polyisoprene 97%; Red: Natural rubber.
 TRIANGLES: Brown: SBS rubber; Red: Polybutadiene cis/trans; Green: Polybutadiene 97%; Blue: Polybutadiene 97.5%.

profile diverges from the others, especially at lower magnetic fields, revealing FFC to be a suitable fingerprinting method.

Isotactic polymers with different molecular weights

The FFC technique is also sensitive to changes in the molecular weight of the polymers. To prove this point, we performed the same experiments described in the previous paragraph on another isotactic PP sample with molecular weight 340K (ISO340K). This polymer was acquired from Sigma-Aldrich (Product Number: 427861). Afterwards, we fitted the corresponding data-sets using the same bi-exponential fitting equation already used for the ISO250K sample. Finally, we compared the results for the fast-relaxing (FIG. 5) and slow-relaxing (FIG. 6) longitudinal magnetization components of the two isotactic samples.

FIG. 5:
Comparison between the fast-relaxing longitudinal relaxation components of the two isotactic samples at different magnetic fields.

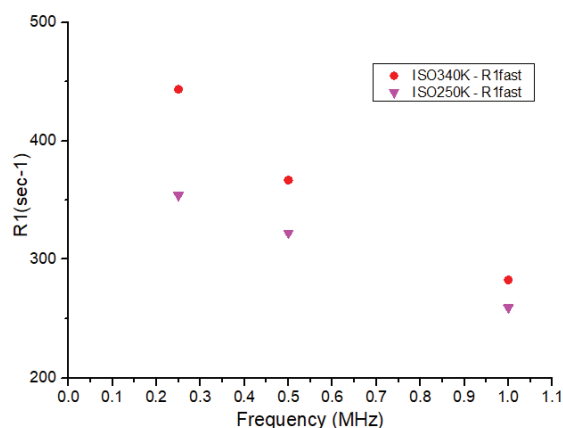
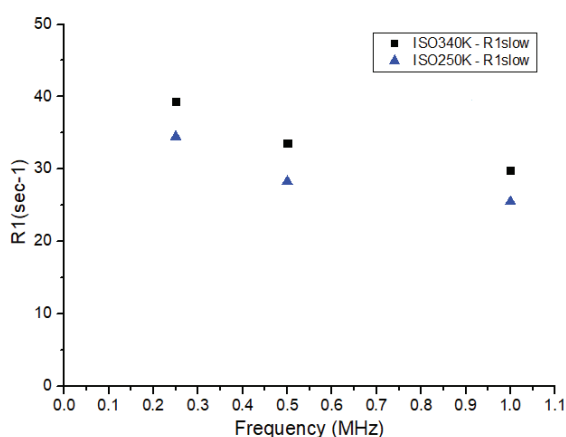


FIG. 6:
Comparison between the slow-relaxing longitudinal relaxation components of the two isotactic samples at different magnetic fields.



Results prove the sensitivity of the NMRD profiles to changes in molecular weight. Analogously to the findings reported in the previous study on the tacticity of PP (FIG. 2 and FIG.3), here as well the difference between the fast-relaxing components of the two isotactic samples is larger than that between the slow-relaxing ones. Moreover, this difference becomes larger as the magnetic field decreases (in agreement with the previous findings shown in FIG. 2). For the slow-relaxing com-

ponents instead (FIG. 6), the difference between the RIs of two isotactic samples seems to be independent (or almost independent) from the magnetic field, at least for the magnetic fields considered.

Furthermore, it is also worth reporting a previous Stellar house-made study in which the FFC technique was successfully exploited to discriminate between three samples of polyethylene glycol differing from each other only by their molecular weights (FIG. 7). Only for magnetic fields lower than about 0.2MHz the NMRD profiles of the samples do not overlap and, moreover, they tend to diverge from each other as the magnetic field decreases.

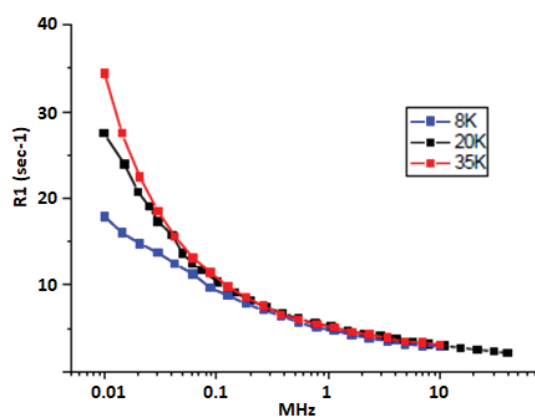


FIG. 7:
Comparison between the slow-relaxing longitudinal relaxation components of the two isotactic samples at different magnetic fields.

Conclusions

In this application note we have shown the potential of the FFC technique to distinguish an isotactic polymer from both an atactic and a 20% adulterated mixture of isotactic polymer at room temperature (25 °C). Furthermore, FFC has been successfully used to discriminate between polymers differing only by their molecular weights. It has been shown that important information can be revealed only at low magnetic fields and it has been discussed that FFC can provide a unique fingerprint for a polymer. Polymer characterization could be developed to become a standard analytical tool and FFC could provide a quality control method for the polymer and plastic industries, with the clear advantage that FFC is a non-destructive method and there is no need to heat the sample to carry out the analysis and no requirement for deuterated solvents.

Notes on Fast Field Cycling NMR Relaxometry

Fast Field cycling (FFC) NMR relaxometry is a low-field magnetic resonance technique which measures the dependence of the spin-lattice relaxation rate R_1 ($= 1/T_1$) on the magnetic field over a wide range of field strengths with just one instrument [1]. FFC is a versatile technique which finds application in many different fields including the polymer industry [2-8].



REFERENCES:

- (1) Kimmich R., Anoardo E., *Field-Cycling NMR Relaxometry*, «Progress in Nuclear Magnetic Resonance Spectroscopy», 44, (2004), 257-320;
- (2) Steele R. M., Korb J. P., Ferrante G., & Bubici S., «New applications and perspectives of fast field cycling NMR relaxometry», *Magnetic Resonance in Chemistry*, 54(6), (2016), 502-509;
- (3) Kimmich R., & Fatkullin N., «Self-diffusion studies by intra- and inter-molecular spin-lattice relaxometry using field-cycling: Liquids, plastic crystals, porous media, and polymer segments», «Progress in nuclear magnetic resonance spectroscopy», 101(2017), 18-50;
- (4) Hofmann M., Kresse B., Heymann L., Privalov A. F., Willner L., Fatkullin N., & Rössler E. A., «Dynamics of a Paradigmatic Linear Polymer: A Proton Field-Cycling NMR Relaxometry Study on Poly (ethylene-propylene)», «Macromolecules», 49(22), (2016), 8622-8632;
- (5) Hofmann M., Gainaru C., Cetinkaya B., Valiullin R., Fatkullin N., & Rössler E. A., «Field-cycling relaxometry as a molecular rheology technique: common analysis of NMR, shear modulus and dielectric loss data of polymers vs dendrimers», «Macromolecules», 48(20), (2015), 7521-7534;
- (6) Flämig M., Hofmann M., Lichtinger A., & Rössler, E. A., «Application of proton field-cycling NMR relaxometry for studying translational diffusion in simple liquids and polymer melts», «Magnetic Resonance in Chemistry», 57(10), (2019), 805-817;
- (7) Flämig M., Hofmann M., & Rössler E. A., (2019), «Field-cycling NMR relaxometry: the benefit of constructing master curves», «Molecular Physics», 117(7-8), 877-887;
- (8) Hofmann M., Kresse B., Privalov A. F., Willner L., Fatkullin N., Fujara F. & Rössler E. A., «Field-cycling NMR relaxometry probing the microscopic dynamics in polymer melts», «Macromolecules», 47(22), (2014), 7917-7929.