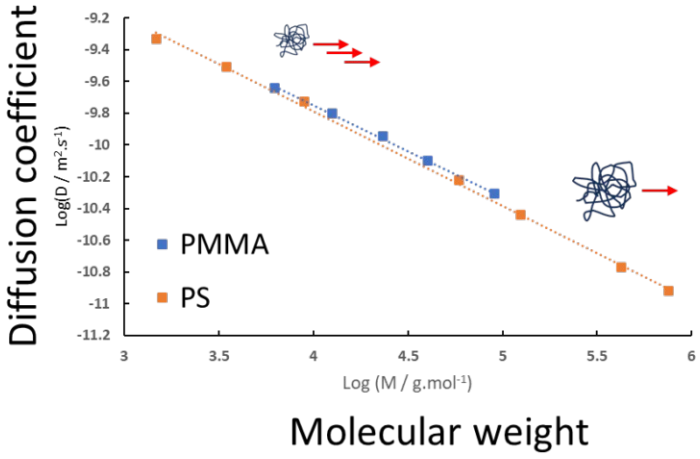
Pulsed Field Gradient NMR for Polymer Molecular Weight and Functionalization Analysis with benchtop NMR

Hélène Freichels, Jürgen Kolz*, Federico Casanova

Magritek GmbH, Philippstr. 8, 52068 Aachen, Germany
**Juergen@magritek.com*

The strength of Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) lies in its ability to separate molecules by hydrodynamic radius while simultaneously resolving chemical structures. The latest generation of benchtop NMR systems offers these capabilities in a compact, user-friendly, and cost-effective manner, making the technique a viable alternative to established methods like size exclusion chromatography.
In this study, benchtop PFG-NMR was employed for molecular weight (MW) determination using Diffusion-Ordered Spectroscopy (DOSY) at 80 MHz. Self-diffusion coefficients (D) of polystyrene and polymethyl methacrylate standards in deuterated chloroform were measured and correlated with MW, achieving measurement times below 10 minutes—significantly improving throughput compared to Size-Exclusion Chromatography (SEC).
To assess accuracy, DOSY-derived MW values were validated against end-group analysis for polyphenylsulfone, demonstrating strong concordance. A similar validation for polysiloxanes further confirmed DOSY's robustness for MW determination. Additionally, DOSY analysis of lignin revealed a well-defined D-MW correlation, highlighting its applicability to both synthetic and natural polymers. Preliminary investigations on chitosan further support its relevance for biopolymer analysis.
Beyond MW determination, PFG-NMR was used to monitor end-group functionalization of poly(ε-caprolactone) (PCL) via the Pulsed Field Gradient-Stimulated Echo (PGSTE) method. This approach effectively resolved reactants and functionalized polymer species, even in cases of spectral overlap, eliminating the need for extensive purification.
Benchtop PFG-NMR provides a compact, cryogen-free platform for rapid, solvent-flexible polymer characterization, offering a viable alternative to high-field NMR for both synthetic and natural macromolecules.

Keywords: benchtop NMR, Pulsed Field Gradient



Plot of log(D) vs log(M) for PMMA (blue) and PS (orange)