Paramagnetic NMR Relaxation Effects in Polymers: Sensitivity Enhancement and Selective Suppression of Signals (^{1}H and ^{13}C PSR Filter)

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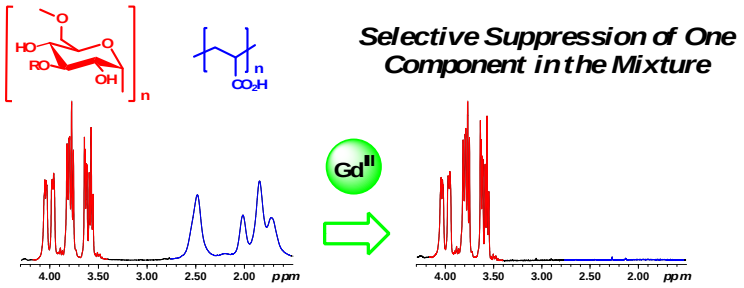
A well-recognized handicap of the NMR spectroscopy of polymers in solution resides on the long time necessary to record quantitative spectra with an acceptable signal-to noise ratio.[1] With the aim of developing faster NMR experiments for polymers, we focused on the use of paramagnetic spin relaxation (PSR) agents as a source of additional relaxation. Application of this strategy to a variety of water soluble polymers/biopolymers [poly-L-lysine, poly(acrylic acid), hyaluronic acid, poly-L-glutamic acid, mannan, dextran, and polyvinylpyrrolidone] and organosoluble polymers (polylactic acid and β-D-1,3-glucan) has been performed by the use of Gd^{III}, Cu^{II}, and Mn^{II} salts. By selecting the appropriate PSR agent concentration, reductions of up 500% in the T_1, and so in the time necessary for recording quantitative NMR spectra of these polymers (sensitivity enhancement), were typically obtained, without any appreciable effect on the spectral line widths and chemical shifts.[2]

Based on the above experiments, it was rationalized that the addition of PSR agents at concentrations higher than those required for the sensitivity enhancement experiments would allow the selective suppression of the ^{1}H and ^{13}C NMR signals of certain species embedded in a polymeric matrix/mixture according to their PSR metal ion complexing ability (1D and 2D PSR filter). Several mixtures illustrating the application of these PSR filters will be presented. Interestingly, in mixtures where PSR filters alone failed in the suppression of certain components (due to their similar sensitivities to Gd^{III}), the use of PSR filters in combination with CPMG sequences (PSR-CPMG filter) successfully resulted in the sequential suppression of certain components.[2]



[1] Bovey, F. A.; Mirau, P. A. *NMR of Polymers*, Academic Press: San Diego, **1996**, pp 17-18 and 358-360.
[2] Fernandez-Megia, E.; Correa, J; Novoa-Carballal, R.; Riguera, R., *J. Am. Chem. Soc.* **2008**, *129*, 15164.