# Diffusion Ordered Spectroscopy (DOSY) experiments

One can measure the diffusion coefficients (D) by NMR, using Pulsed Field Gradients (PFG). After a 90° pulse on *x*, the magnetization is on the *y* axis. A pulse field gradient along the *z*-axis will encode the positions of the spins as phase. At this time, no signal can be observed since the magnetization has fanned out in the *xy* plane. A subsequent gradient of the same strength and duration, but of opposite direction, refocuses the magnetization on the *y* axis, as long as the spins kept their position on the *z*-axis. The faster the diffusion, and the stronger the gradients, the larger the loss of signal is. Actual pulse sequences will keep the magnetization on the *z*-axis between the gradients for the diffusion time.

For this experiment you want to use a higher field instrument and an indirect detection probe (i3c with id3).

Tune the probe, then take a proton spectrum in experiment 1, with at=2, d1=3 and pw=pw90 .

Go to the top menu Edit and drag to Move FID. Move the FID from experiment 1 to experiment 2, and join experiment 2. In the Process tab click the top button Transform to get a copy of the spectrum in experiment 1.

In the top menu Experiments drag to Convert current parameters to do – DOSY Experiments – 2D DOSY with Convection Compensation – Bipolar Pulse Pair Stimulated Echo.

In the Acquire – Defaults tab click Setup Coarse Gradient array. Make nt=1 ss=2, if the concentration of the sample allows it. Next you will acquire 7 spectra with increasing gradient strength, with the purpose of adjusting the diffusion gradient length (0.5 to 4 ms) and the diffusion delay (20-400 ms). Increasing any of these two reduces the intensity of the signal in the spectrum with the highest gradient strength. Adjust these so that the last spectrum has 50-20 % of the intensity of the first.

With these parameters, proceed to acquiring more field strength increments each of more transients, to improve the accuracy of D. Set the number of increments to 15-30, then click Set up DOSY using conditions above. Set the number of transients to 4-64, then the number of dummy scans ss to 8-16. In Acquire - Flags set Block size to1 and check Acquire arrays by blocks. Start the acquisition.

To process the data start by defining the integrals for baseline correction, then in the Process – DOSY Process tab click Baseline correct all spectra. Define now integrals for the peaks you want in the DOSY analysis. They should be peaks solely from the compound, not overlapping any signals from other contaminants. Check correct for non-uniform gradients and use integral values, then click Calculate full DOSY. The result will appear as a 2D plot, Diffusion Coefficient *vs*. Frequency. To see the errors for a particular integral region, input its number in the peak # box and click show fit for the peak above. To reprocess or to acquire with the same parameters, click Recall original NMR spectra.

### Application to Determination Molecular Weight of Polymers.

Select a set (3-5) of GPC standards of known MW and a deuterated solvent that will dissolve both the polymer and the standards. The samples should be as diluted as possible and still have a good signal to noise ratio. Try 10 mg/ml. Run the DOSY experiment for the polymer and determine its diffusion coefficient, D. Do the same for one of the standards, then move to the next standards trying to bracket the D of the polymer. Determine *k* and $\nu$ in the equation $D = kM^{-\nu}$ (1) and use them to calculate the MW of the polymer. You can use this Excel spreadsheet. In Solver, minimize D11 on variables D1, D2.

(1) Chen, A.; Wu, D.; Johnson, C. S. *J. Am. Chem. Soc.* 1995, **117**,7965−7970.